β-Fission of 9-Decalinoxyl Radicals: Reversible Formation of 6-Ketocyclodecyl Radical

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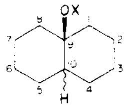
Rearrangement at 0 °C of *trans*-9-decalinyl hypobromite ($\mathbf{1}_{trans}$, X = Br), formed by the interaction of $\mathbf{1}_{trans}$ (X = H) with bromine and silver acetate or mercuric oxide, gives 6-bromocyclodecanone (**4**, X = Br) whereas the same reaction at 81 °C gives 2-(4-bromobutyl)cyclohexanone (**6**, X = Br). The cis isomer ($\mathbf{1}_{cis}$, X = Br) behaves similarly. The relative yields of the nitroso dimers, **11**, **12**, and **13**, formed by photolysis of $\mathbf{1}_{cis}$ (X = NO) and $\mathbf{1}_{trans}$ (X = NO), also depend on the reaction temperature. Reduction of 6-bromocyclodecanone (**4**, X = Br) with tributylstannane in high concentration gives mainly *cis*- and *trans*-9-decalinol, with the former predominating. These results indicate (i) that 9,10-bond fission of the 9-decalinoxyl radicals, $\mathbf{2}_{cis}$ and $\mathbf{2}_{trans}$, is rapid but reversible, (ii) that 1,9-bond fission of $\mathbf{2}_{cis}$ and $\mathbf{2}_{trans}$ is relatively slow and is essentially irreversible under the conditions used here, and (iii) that ring closure of the radical (**5**) favors formation of the cis product ($\mathbf{2}_{cis}$).

Although polar effects[1,2] can also play an important role, β-fission reactions of *tert*-alkoxy radicals usually conform to the generalisation that the relative rates of bond cleavage reflect the stabilities of the products; the reaction affords tertiary radicals in preference to secondary, and secondary in preference to primary.[1-4] Contrary to expectation, the 9-decalinoxyl radical ($\mathbf{2}_{trans}$), when generated by thermolysis of the hypoiodite ($\mathbf{1}_{trans}$, X = I)[5] or the hydroperoxide ($\mathbf{1}_{trans}$, X = OH)[6] or by ferrous ion reduction of the latter,[6] gives products (e.g., **6**, X = I) derived from the primary radical (**3**), the less stable of the two possible products of β-fission of $\mathbf{2}_{trans}$. Since work already in progress in these laboratories[7] when Macdonald and O'Dell[5] disclosed the results of their experiments with the hypoiodite ($\mathbf{1}_{trans}$, X = I) had shown that photolysis of the analogous hypobromite ($\mathbf{1}_{trans}$, X = Br) follows the alternative direction, we decided to study this system more thoroughly. In the present paper we examine the behavior of the cis- and trans-isomers of the 9-decalinoxyl radical generated from a variety of precursors and present a mechanistic rationale involving a delicate interplay of kinetic and thermodynamic factors.



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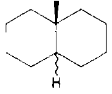

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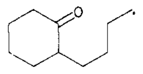

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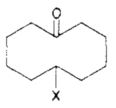

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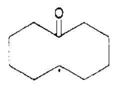

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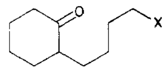

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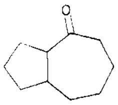

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Table I. Homolysis of 9-Decalinyl Hypobromites in Benzene

isomer	T, °C	metal salt	relative yields, % 4 (X = Br)	6 (X = Br)
trans	0	AgOAc	100	0
cis	0	AgOAc	95	5
trans	0	AgOAc/HgBr	100	0
cis	0	HgO	100	0
trans	50	AgOAc	80	20
cis	50	AgOAc	80	20
cis	50	HgO	85	15
trans	65	AgOAc	40	60
cis	65	AgOAc	35	65
cis	65	AgOAc	40	60
trans	81	HgO	5	95
cis	81	HgO	10	90

Results and Discussion

Our initial experiments confirmed the results of earlier work[5,7] on the decomposition of decalinyl hypohalites. Thus, treatment of *trans*-9-decalol ($\mathbf{1}_{trans}$, X = H) with mercuric oxide and iodine in boiling carbon tetrachloride as described by Macdonald and O'Dell[5] gave only 2-(4-iodobutyl)cyclohexanone (**6**, X = I) whereas photolysis at 0 °C of the mixture formed by interaction of $\mathbf{1}_{trans}$ (X = H) with bromine and silver acetate in benzene afforded 6-bromocyclodecanone (**4**, X = Br) as the sole ring-opened product. The assignment of structure to **4** (X = Br) was based on its ^{1}H and ^{13}C NMR spectral properties and was confirmed by its conversion into bicyclo[5.3.0]decan-2-one (**7**) upon treatment with ethanolic potassium hydroxide.

Next, we sought to establish the effect, if any, of the nature of the metal salt and the halogen upon the direction of ring opening. When Macdonald and O'Dell's procedure[5] was conducted with bromine in place of iodine the only product isolated was that (**6**, X = Br) arising from fission of the 1,9-bond. A similar result was obtained when bromine was added to the decalol ($\mathbf{1}_{trans}$, X = H) and mercuric oxide in boiling benzene. However, addition of mercuric bromide had no effect upon the reaction of $\mathbf{1}_{trans}$ (X = H) with bromine and silver acetate at 0 °C; the sole product was that (**4**, X = Br) arising from 9,10-bond fission.

These results suggested that the nature of the metal salt was immaterial, and that the outcome of the reaction was

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[1] Bacha, J. D.; Kochi, J. K. *J. Org. Chem.* **1965**, *30*, 3272. Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2333; **1964**, *86*, 3368.

[2] For a review of alkoxy radical fragmentation see: Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, Chapter 23, p 665.

[3] Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. *J. Org. Chem.* **1963**, *28*, 55. Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

[4] For recent examples of β-fission of alkoxy radicals see: Janjatovic, J.; Majerski, Z. *J. Org. Chem.* **1980**, *45*, 4892. Barton, D. H. R.; Motherwell, R. S. H.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1*, 1981, 2363. Suginome, H.; Isayama, S.; Maeda, N.; Furusaki, A.; Katayama, C. *J. Chem. Soc.*, Perkin *Trans. 1* 1981, 2963. ySchreiber, S. L. *J. Am. Chem. Soc.* **1980**, *102*, 6163.

[5] Macdonald, T. L.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1501.

[6] Holmquist, H. E.; Rothrock, H. S.; Theobald, C. W.; Englund, B. E. *J. Am. Chem. Soc.* **1956**, *78*, 5339.

[7] Gara, W. B., Honors Thesis, Organic Chemistry Department, University of Adelaide, 1966.

0022-3263/83/1948-4718$01.50/0

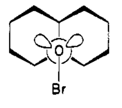
Table II. Photolysis of 9-Decalinyl Nitrite (1, X = NO)

isomer	solvent	T, °C	nitroso dimers total, %	11, %[a]	12, %[a]	13, %[a]	9,10-bond fission, %[a]	decalinols cis/trans
cis	CH_2Cl_2	−60	13	66	4	30	81	50:1
trans	CH_2Cl_2	−60	39	88	0	12	94	ND[b]
cis	CH_2Cl_2	0	30	16	42	42	37	7.3:1
trans	CH_2Cl_2	0	40	2	73	25	15	ND[b]
cis	C_6H_6	0	18	10	50	40	30	3.4:1
trans	C_6H_6	0	37	0	79	21	12	ND[b]
cis	CH_2Cl_2	25	36	3	67	30	18	7.2:1
cis	C_6H_6	25	28	1	68	31	17	2.8:1

[a] Relative yields. [b] Not determined.

controlled by the effect of temperature upon the decomposition of the initially formed hypohalite. An early attempt to verify this hypothesis by heating solutions of the hypobromite formed by the use of silver acetate–bromine at 0 °C gave erratic results, probably because the homolytic reaction was complete before the mixture had reached the temperature of the bath. However, a series of experiments in which bromine was added to *trans*-9-decalol and silver acetate or mercuric oxide at various temperatures (see Table I) showed that the ratio of 1,9-bond fission to 9,10-bond fission is very small at 0 °C but rises dramatically with an increase in temperature.

It has been suggested recently[8] that the direction of β-fission of alkoxy radicals is influenced by stereoelectronic effects; the reaction occurs most readily when the bond undergoing cleavage and an adjacent oxygen lone pair in the radical precursor can assume a trans antiperiplanar relationship. Inspection of a model of the most stable conformer (8) of the trans hypobromite (1_{trans}, X = Br) reveals that this relationship exists for the 1,9- and 8,9-bonds but not for the 9,10-bond.[9]



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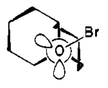

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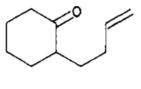
Models of the cis hypobromite (1_{cis}, X = Br) show that there are two low-energy conformers, one of which (9) is correctly disposed to favor both 1,9- and 9,10-bond fission. If these stereoelectronic hypotheses are correct we should expect, therefore, that the cis hypobromite (1_{cis}, X = Br) will exhibit a greater preference for 9,10-bond fission than its trans isomer (1_{trans}, X = Br). However, when the cis alcohol (1_{cis}, X = H) was treated with silver acetate and bromine in benzene at various temperatures, the relative yields of 9,10- and 1,9-fission products were the same, within experimental error, as those obtained from the trans alcohol (1_{trans}, X = H) under identical conditions (see Table I). These results, and the fact that hypoiodites behave similarly to the corresponding hypobromites, although they should be subject to a higher degree of conformational preference, suggest that stereoelectronic effects in the radical precursor are unimportant in determining the direction of ring opening of decalinoxyl radicals (2).

The reduction of *tert*-alkyl hydroperoxides with cuprous or ferrous salts provides an unambiguous method for the generation of alkoxy radicals.[12] When *trans*-9-decalin hydroperoxide (1_{trans}, X = OH) was heated with cupric acetylacetonate or cupric octanoate in boiling benzene the only product isolated (75%) was 2-(3-butenyl)cyclohexanone (**10**), the formation of which must involve cupric ion oxidation[13] of the radical (**3**) formed by 1,9-bond fission. Similarly, **10** was obtained upon addition of ferrous ion to a mixture of the hydroperoxide (1_{trans}, X = OH) and cupric acetate in acetic acid–methanol at 0 °C. However, treatment of the hydroperoxide (1_{trans}, X = OH) in ethanol with ferrous sulfate alone gave the expected product (**6**, X = H) of one-electron reduction of the radical (**3**).

In view of the indications that reaction temperature is the dominant factor determining the direction of β-fission of decalinoxyl radicals we decided to examine the photolysis of the nitrites (**1**, X = NO) over a wide range of temperature. When the trans isomer (1_{trans}, X = NO), prepared by treatment of the alcohol (1_{trans}, X = H) with nitrosyl chloride, was irradiated in dichloromethane solvent with UV light at 0 °C it afforded three stable nitroso dimers which were separated chromatographically. The UV spectrum of the most polar of these dimers showed the intense absorption at 292 nm characteristic of this class of compound,[14] the infrared spectrum contained a carbonyl peak, the ^1H NMR spectrum included a two-proton triplet resonance at δ 4.2, and the ^{13}C NMR spectrum, which contained ten distinct resonances, was similar to those of **6** (X = Br or I). These spectral data are consistent with the structure (**12**).



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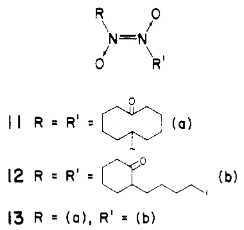

The least polar dimer showed only six distinct resonances in its ^{13}C NMR spectrum and gave other spectral data consistent with its formulation as the dimer (**11**) of 6-nitrosocyclodecanone. The product of intermediate polarity showed spectral features in common with both of the other two dimers in harmony with its formulation as the mixed dimer (**13**).

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[8] Bensadoun, N.; Brun, P.; Casanova, J.; Waegell, B. *J. Chem. Res. Synop.* **1981**, 236 and references cited therein.

[9] In structures 8 and 9 we have followed the original literature[8] and have represented the two oxygen lone pairs as occupying sp^3 orbitals of equal energy. It is more probable that one pair occupies a p-type orbital of relatively high energy, while the other residues in a low-energy s-type orbital.[10] This, however, makes little difference to the stereoelectronic argument.[11]

[10] David, S.; Eisenstein, O.; Hehre, W. J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 3806. Sweigart, D. A. *J. Chem. Educ.* **1973**, *50*, 322 and references cited.

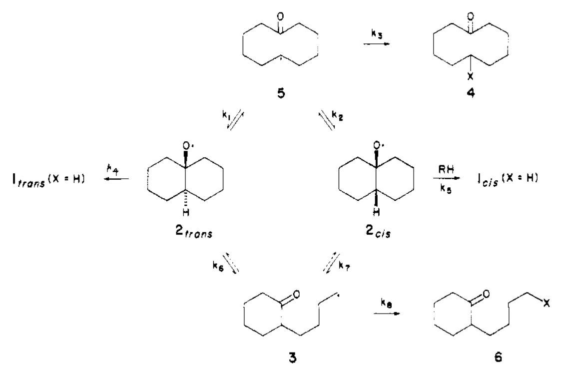
[11] For a similar example see: Beckwith, A. L. J.; Easton, C. J. *J. Am. Chem. Soc.* **1981**, *103*, 615.

[12] For pertinent reviews see: Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 11, p 591. Hiatt, R. In "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1973; Vol. 1. Chapter 1.

[13] Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843 and references cited therein.

[14] Kabasakalian, P.; Townley, E. R. *J. Am. Chem. Soc.* **1962**, *84*, 2711.

Scheme I



From the yields of the three dimers it is possible to determine the relative yields of 1,9- and 9,10-fission products. The results are given in Table II together with those for similar experiments. Although the yields of dimers were low and the results somewhat erratic, the trend is clear; low temperatures favor 9,10-bond fission, but 1,9-bond fission becomes increasingly important as the temperature is raised. The relative extent of 1,9- and 9,10-bond fission is approximately the same in benzene or dichloromethane.

Photolysis of the cis nitrite ($\mathbf{1}_{\mathrm{cis}}$, X = NO) gave very similar results. Both isomers of the nitrite also afforded 9-decalinol presumably by hydrogen-atom transfer to the radicals $\mathbf{2}_{\mathrm{cis}}$ and $\mathbf{2}_{\mathrm{trans}}$ from dichloromethane, when it was used as solvent, or from starting material. Photolysis of the trans nitrite ($\mathbf{1}_{\mathrm{trans}}$, X = NO) gave mainly the trans alcohol ($\mathbf{1}_{\mathrm{trans}}$, X = H) but the isomer ratio was not accurately determined. However GLC analysis of the 9-decalinol formed from the cis nitrite ($\mathbf{1}_{\mathrm{cis}}$, X = NO) showed that the cis/trans ratio is large at -60 °C but decreases with an increase in reaction temperature. Also it is smaller for photolyses conducted in benzene than for those in dichloromethane.

All of the experimental observations are consistent with the mechanism depicted in Scheme I. The salient features of the mechanism are (i) that each isomer, $\mathbf{2}_{\mathrm{cis}}$ and $\mathbf{2}_{\mathrm{trans}}$, of 9-decalinoxyl radical undergoes fast, but reversible 9,10-bond fission, and (ii) that 1,9-bond fission is slower than 9,10-bond fission but is essentially irreversible under the conditions used in these experiments.

The major evidence for the reversibility of 9,10-bond fission comes from the formation of *trans*-9-decalinol ($\mathbf{1}_{\mathrm{trans}}$, X = H) by photolysis of the cis nitrite ($\mathbf{1}_{\mathrm{cis}}$, X = NO). The only plausible pathway for interconversion of the isomeric decalinoxyl radicals, $\mathbf{2}_{\mathrm{cis}}$ and $\mathbf{2}_{\mathrm{trans}}$, is through the ring-opened radical (**5**).[15]

The distribution of stable products from the system $\mathbf{2}_{\mathrm{trans}} \rightleftharpoons \mathbf{5} \rightleftharpoons \mathbf{2}_{\mathrm{cis}}$ will depend on how effectively trapping reactions compete with the establishment of equilibrium. For example, the large cis/trans ratio for formation of 9-decalinol by photolysis of the cis nitrite ($\mathbf{1}_{\mathrm{cis}}$, X = NO) in dichloromethane reflects the relative efficiency of hydrogen-atom transfer from the solvent, i.e., k_5[RH] must be at least of comparable magnitude with k_{-2}. In benzene hydrogen-atom transfer is less efficient and the cis/trans ratio for 9-decalinol is reduced.

Direct evidence for the reversibility of formation of the radical (**5**) was obtained when the bromo compound (**4**, X = Br) was heated with tributylstannane in benzene at 60 °C. Analysis of the mixture by GLC showed the relative yields of products to be: *cis*-9-decalinol ($\mathbf{1}_{\mathrm{cis}}$, X = H), 75%; *trans*-9-decalinol ($\mathbf{1}_{\mathrm{trans}}$, X = H), 20%; and cyclodecanone (**4**, X = H, 4%. The low yield of the last is significant in that it indicates that cyclisation of **5** is much faster than hydrogen-atom transfer from stannane even under conditions of high stannane concentration ([Bu_3SnH] ≈ 1.3 M). It we assume that the decalinoxyl radicals, $\mathbf{2}_{\mathrm{trans}}$ and $\mathbf{2}_{\mathrm{cis}}$, are efficiently trapped by stannane, and that k_H, the rate constant for formation of **4** (X = H) from **5**, has a normal value for a secondary alkyl radical ($k_H \approx 4.6 \times 10^6$ l mol^{-1} s^{-1} at 60 °C),[16] it is possible to deduce values of k_1 and k_2. Application of the usual integrated rate equation[17] gives $k_1 \approx 2 \times 10^7$ s^{-1} and $k_2 \approx 6 \times 10^7$ s^{-1} at 60 °C. Such high values for ring closure onto a carbonyl group appear to be without precedent. Presumably they reflect favorable energy and entropy factors associated with transannular bond formation.

The observation that the rate of formation of the cis radical ($\mathbf{2}_{\mathrm{cis}}$) is greater than that for the trans ($\mathbf{2}_{\mathrm{trans}}$), i.e., $k_2 > k_1$, is also unexpected since the relative order of thermodynamic stability of the two radicals is expected to be $\mathbf{2}_{\mathrm{trans}} > \mathbf{2}_{\mathrm{cis}}$. Possibly this outcome of the ring-closure reaction reflects the conformational preference of **5**. In the crystalline state, cyclodecane-1,6-dione, a reasonable analogue for **5**, assumes a *trans*-decalin-like conformation.[18] However, in solution it takes up a different conformation, the nature of which has not yet been rigorously defined.[18] Inspection of models suggests that a *cis*-decalin-like conformation should be of relatively low energy.

When 6-bromocyclodecanone (**4**, X = Br) was heated with tributylstannane at low concentration ([Bu_3SnH] ≈ 0.05 M) no cyclodecanone was detected. Under these conditions the trapping of **5** by the stannane is too slow to compete effectively with ring closure. The product mixture was shown by gas chromatography to contain *cis*-9-decalinol, *trans*-9-decalinol, and 2-butylcyclohexanone (**6**, X = H) in the ratio 1:1:2. The formation of approximately equal amounts of the two epimers of 9-decalinol probably indicates that epimerisation of $\mathbf{2}_{\mathrm{cis}}$ via **5** is sufficiently fast to compete with its reaction with stannane. However, it could also indicate that $\mathbf{2}_{\mathrm{cis}}$ is converted into **3** more rapidly than is $\mathbf{2}_{\mathrm{trans}}$, i.e., $k_7 > k_6$. Our present results do not allow these two possibilities to be distinguished.

Treatment of the bromo ketone (**6**, X = Br) with tributylstannane in low concentration ([Bu_3SnH] = 0.02 M) at 60 °C afforded mainly 2-butylcyclohexanone (**6**, X = H). A small amount (<10%) of a complex mixture was formed which may have contained some 9-decalinol although neither isomer was positively identified. Application of the usual procedure shows that if the yield of cyclic products is <5%, then $(k_{-6} + k_{-7})/k_8 < 2.2 \times 10^{-4}$ M. Since $k_H \approx 4.6 \times 10^6$ l mol^{-1} s^{-1} at 60 °C,[16] the sum of the rate constants ($k_{-6} + k_{-7}$) must be less than 1×10^3 s^{-1}. In making this deduction we have assumed that the trapping of 9-decalinoxyl radicals, $\mathbf{2}_{\mathrm{cis}}$ and $\mathbf{2}_{\mathrm{trans}}$, by stannane is sufficiently rapid to prevent the equilibrium between them and **5** from becoming fully established. Further detailed kinetic work is required to verify this assumption.

The final outcome of any reaction involving some or all of the mechanistic pathways depicted in Scheme I will depend upon the competition between the trapping of intermediate radicals and their interconversion. Since the

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[15] For a recent example of epimerisation of an alkoxy radical through consecutive ring opening and ring closure see: Nickon, A.; Ferguson, R.; Bosch, A.; Iwadare, T. *J. Am. Chem. Soc.* **1977**, *99*, 4518.

[16] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

[17] Beckwith, A. L. J.; Phillipou, G. *J. Chem. Soc., Chem. Commun.* **1973**, 280.

[18] Alvik, T.; Borgen, G.; Dale, J. *Acta Chem. Scand.* **1972**, *26*, 1805.

rates of trapping will depend not only upon the magnitudes of the appropriate rate constants, k_3, k_4, k_5, and k_8, but also upon the concentration of the trapping reagent, it is not surprising that the results of nitrite photolyses are very different from those of hypohalites. The relatively high proportion of 1,9-fission products from the former indicate a low rate of trapping of the radical **5**. Presumably the stationary concentration of the trapping agent, nitric oxide, remains very low throughout the reaction. However, in hypohalite photolyses at <50 °C radical **5** is clearly efficiently trapped. Not only does k_3 have a high value,[19] but the concentration of the trapping agent, the hypohalite itself, remains relatively high throughout the reaction.

The formation of the 1,9-fission product (**6**, X = H) by ferrous ion reduction of the hydroperoxide ($\mathbf{1}_{\text{trans}}$, X = OH) at ambient temperature indicates that the possible trapping reactions, viz electron transfer from Fe^{2+} or hydrogen-atom transfer from ethanol solvent, must be relatively slow. Similarly, the formation of **10** by treatment of the hydroperoxide ($\mathbf{1}_{\text{trans}}$, X = OH) with ferrous sulfate and cupric acetate in acetic acid and methanol at 0 °C suggests that the reaction of the radical (**5**) with cupric ion is relatively slow. Other evidence,[13] however, indicates that cupric ion oxidation of radicals is remarkably rapid. Perhaps in this case Cu^{2+} forms a complex with the radical ($\mathbf{2}_{\text{trans}}$), the β-fission of which then falls under stereoelectronic control.

The fact that 1,9-fission begins to predominate above about 50 °C even in hypohalite reactions suggests that k_6 and k_7 have relatively high values for their activation energies and preexponential terms. This is consistent with values of Arrhenius parameters for β-fission reactions of simple alkoxy radicals to afford primary alkyl radicals.[20] Our results also suggest that the activation energy for the 9,10-bond fission of $\mathbf{2}_{\text{cis}}$ or $\mathbf{2}_{\text{trans}}$ is, as expected for reactions producing a secondary radical,[20] relatively low. However, it is probable that log A is also relatively low, since 9,10-bond fission does not markedly increase the configurational mobility, and hence the entropy, of the system.

Finally, it is noteworthy that the decomposition of 9-decalinyl hypohalites (**1**, X = halogen) can be directed, through proper attention to experimental conditions, to afford exclusively *either* 9,10- or 1,9-bond fission products, which can, in turn, be converted into bicyclo[5.3.0]decane or spiro[4.5]decane systems. Reactions of this general type, therefore, appear suitable for synthetic exploitation.

Experimental Section

General Procedures. Melting points and boiling points are uncorrected. Ultraviolet spectra and infrared spectra were recorded on a Varian DMS 90 spectrophotometer and a Perkin-Elmer 457 spectrometer respectively. ^1H NMR spectra were recorded at 100 MHz on a JEOL-MH-100 spectrometer, and at 200 MHz on a JEOL JNM-FX-200 Fourier transform spectrometer, which was also used to record ^{13}C NMR spectra. All NMR spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were recorded on a V.G. Micromass 7070 system at 70 eV. Merck Kieselgel 60 F-254 precoated plates were used for TLC analysis. Analytical HPLC was conducted with a Waters M6000A pump, a Waters Radpack silica column, and a Waters refractive index detector; the flow rate was 1.5 mL/min. Preparative HPLC separations were achieved on a Whatman M9 column (9 cm × 50 cm) with a flow rate of 7 mL/min.

Materials. The two isomers of 9-decalinol $\mathbf{1}_{\text{cis}}$ and $\mathbf{1}_{\text{trans}}$ (X = H) were prepared from a mixture of octalins[21] as previously described[22] except that the crude products were subjected to chromic acid oxidation to convert secondary alcohols into ketones,[23] and the required decalinols were then isolated by chromatography on Sorbsil. *trans*-9-Decalinyl hydroperoxide ($\mathbf{1}_{\text{trans}}$, X = OH) and its acetate ($\mathbf{1}_{\text{trans}}$, X = OAc) were prepared as described previously, as were authentic samples of 2-(4-bromobutyl)cyclohexanone,[24] 2-(3-butenyl)cyclohexanone,[25] and bicyclo[5.3.0]decan-2-one.[26]

Formation and Homolysis of 9-Decalinyl Hypohalites. A. Silver acetate (1.08 g, 6.5 mmol) and *trans*-9-decalinol (1.0 g, 6.5 mmol) in deaerated benzene (15 mL) were stirred at 0 °C in the dark under nitrogen while bromine (1.04 g, 6.5 mmol) in benzene (5 mL) was added during 10 min. The mixture was stirred in the dark at 0 °C for 1 h, then filtered and exposed to sunlight for 15 min, by which time the orange color had faded. Chromatography of the crude product on silica gel with dichloromethane as solvent afforded *trans*-9-decalinol, identified by GLC, and *6-bromocyclodecanone* (1.1 g, 75%), bp 95 °C (0.3 mm), which slowly formed a crystalline solid, mp 30–35 °C; IR (film) 1700 cm^{-1}; ^1H NMR δ 1.2–2.0 (complex m, 12 H), 2.0–2.6 (complex m, 4 H, CH_2COCH_2), 4.20 (1 H, quintet, J = 6 Hz, CHBr); $[^1H]^{13}C$ NMR δ 22.9 (t, 2 C), 24.3 (t, 2 C), 35.9 (t, 2 C), 42.1 (t, 2 C), 53.3 (d), 214.0 (s); mass spectrum, m/e 234 (1%), 232 (1) 153 (33), 151 (11), 135 (100), 95 (13), 83 (17), 81 (21), 79 (13), 69 (33), 67 (38), 55 (78), 41 (40). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.5; H, 7.4; Br, 34.3. Found: C, 51.9; H, 7.3; Br, 34.8.

B. A mixture of *trans*-9-decalinol (383 mg, 2.5 mmol), yellow mercuric oxide (1.65 g, 7.6 mmol) and benzene (10 mL) was stirred and refluxed under nitrogen while a solution of bromine (1.16 g, 7.3 mmol) in benzene (40 mL) was added during 1 h. The mixture was then cooled and filtered, and the filtrate was chromatographed on silica gel with dichloromethane as solvent to afford **4** (X = Br) (ca. 5%) and 2-(4-bromobutyl)cyclohexanone (310 mg, 53%): bp 95–100 °C (0.4 mm); IR (film) 1705 cm^{-1}; ^1H NMR δ 1.5–2.0 (complex m, 12 H) 2.0–2.6 (complex m, 3 H, $CHCOCH_2$), 3.40 (t, J = 7 Hz, 2 H, CH_2Br); $[^1H]^{13}C$ NMR δ 25.0 (t), 25.7 (t), 27.9 (t), 28.5 (t), 32.9 (t), 33.8 (t, 2C), 42.0 (t), 50.5 (d), 213.1 (s); mass spectrum, m/e 234 (0.08%), 233 (0.06), 232 (0.06), 231 (0.05), 111 (17), 98 (100), 55 (20). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.5; H, 7.4; Br, 34.3. Found: C, 52.0; H, 7.4; Br, 34.6.

C. Repetition of the above experiments with *cis*-9-decalinol afforded the same products in similar yields.

D. Bromine (0.51 g, 3.2 mmol) in benzene (10 mL) was added during 30 min to a stirred mixture of *trans*-9-decalinol (230 mg, 1.46 mmol), HgO (700 mg, 3.2 mmol), and benzene (10 mL) in the dark. The mixture was then refluxed for 30 min, cooled, filtered, and washed with water. Evaporation of the solvent afforded a mixture of **4** (X = Br) and **6** (X = Br) in the ratio of 1:2, pure samples of which were separated by HPLC.

E. A mixture of *trans*-9-decalinol (113 mg, 0.73 mmol), AgOAc (123 mg, 0.74 mmol), and deaerated benzene (2.5 mL) was stirred under nitrogen in a bath at 0 °C while bromine (118 mg, 0.74 mmol) in benzene (0.5 mL) was added during 10 min. After being stirred at 0 °C under illumination by a tungsten lamp for 1 h the mixture was filtered and the residue was washed with ether. The filtrate was washed with sodium bicarbonate solution and evaporated to afford an oil which was analyzed by NMR. The experiment was repeated at various temperatures and with *cis*-9-decalinol. The results are presented in Table I.

F. *cis*-9-Decalinol (88 mg, 0.57 mmol) and HgO (260 mg, 1.2 mmol) were treated with bromine (192 mg, 1.2 mmol) in benzene at 50 °C according to the general procedure E. The experiment was repeated at various temperatures and with *trans*-9-decalinol. The results are presented in Table I.

Formation and Photolysis of 9-Decalinyl Nitrites (1, X = NO). A. When nitrosyl chloride was slowly passed into a solution of *trans*-9-decalinol (540 mg) in pyridine (5 mL), the

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mixture initially turned green and then became dark red. Water was then added and the mixture was extracted with pentane. The pentane solution was washed with cold dilute sulfuric acid and with water, dried, and evaporated to give the trans nitrite (1_{trans}, X = NO) as a pale green–yellow oil (700 mg) which solidified below 10 °C; IR (film) 1625 cm^{-1}; UV (hexane) 233, 341, 354, 367, 383, 400 nm; $[^1H]^{13}C$ NMR δ 21.1 (t, 2 C), 26.1 (t, 2 C), 28.1 (t, 2 C), 38.1 (t, 2 C), 44.7 (d), 84.3 (s).

A sample (240 mg) of this nitrite was dissolved in deaerated dichloromethane (25 mL) in a Pyrex flask, and the solution was then kept at 0 °C under nitrogen while being irradiated with a 250-W high-pressure mercury lamp for 45 min, by which time the UV spectrum of the mixture showed intense absorption at 292 nm but indicated that all the nitrite had been consumed. The mixture was then evaporated in vacuo and the residue was chromatographed on silica gel with diethyl ether–dichloromethane mixtures as solvent to afford 9-decalinol (85 mg) and three nitroso dimers which were further purified by HPLC.

The least polar dimer (11) (7 mg, 3%) was a crystalline solid; IR (Nujol) 1705 cm^{-1}; UV (hexane) 292 nm; ^1H NMR δ 1.0–3.1 (m, 32 H), 5.74 (quintet, *J* = 6 Hz, 2 H, CHN); $[^1H]_{13}C$ NMR δ 23.0 (t, 8 C), 27.9 (t, 4 C), 41.5 (t, 4 C), 64.2 (d, 2 C), 213.8 (s, 2 C); mass spectrum, *m/e* (relative intensity) 166 (8), 153 (16), 151 (32), 135 (100), 93 (34), 67 (62), 55 (63), 41 (47).

The most polar dimer (**12**) crystallized from ether–pentane in colorless needles (65 mg, 27%), mp 70–74 °C; IR ($CHCl_3$) 1705 cm^{-1}; UV (hexane) 292 nm; ^1H NMR δ 1.2–2.4 (m, 30 H), 4.24 (t, *J* = 7 Hz, 4 H, CH_2N); $[^1H]^{13}C$ NMR δ 24.3 (t, 2 C), 25.0 (t, 2 C), 25.2 (t, 2 C), 27.9 (t, 2 C), 28.8 (t, 2 C), 33.9 (t, 2 C), 42.1 (t, 2 C), 50.4 (d, 2 C), 58.7 (t, 2 C), 212.9 (s, 2 C); mass spectrum, *m/e* (relative intensity) 166 (11), 153 (15), 98 (100), 55 (65), 41 (50).

The dimer (**13**) of intermediate polarity was a crystalline solid (21 mg, 9%); IR (Nujol) 1705 cm^{-1}; UV (hexane) 292 nm; ^1H NMR δ 1.0–3.1 (m, 31 H), 4.26 (t, *J* = 7 Hz, 2 H, CH_2N), 5.70 (quintet, *J* = 6 Hz, 1 H, CHN); mass spectrum, *m/e* (relative intensity) 220 (2), 205 (7), 166 (19), 153 (19), 151 (17), 135 (85), 98 (73), 93 (44), 69 (54), 67 (80), 55 (100), 41 (80).

B. A sample (115 mg) of the trans nitrite (1_{trans}, X = NO) was dissolved in dichloromethane (10 mL) and irradiated at –60 °C for 40 min. The total yield of nitroso dimers (39%) was calculated from the optical density of the mixture at 292 nm, while the relative yields of **11**, **12**, and **13** were determined by HPLC with hexane–ethyl acetate (2:5). The results of this and related experiments are presented in Table II.

C. Treatment of *cis*-9-decalinol with nitrosyl chloride as described above gave the cis nitrite (1_{cis}, X = NO) as a pale yellow–green oil; UV (pentane) 230, 342, 354, 368, 384, 400 nm; $[^1H]^{13}C$ NMR δ 22.6 (t, 4 C), 27.8 (t, 2 C), 34.3 (t, 2 C), 39.9 (d), 87.1 (s). Samples of the nitrite were photolyzed as described above and analyzed by HPLD to give the results presented in Table II.

Metal Ion Catalyzed Reactions of *trans*-9-Decalinyl Hydroperoxide (1_{trans}, X = OH). A. A mixture of cupric acetylacetonate (70 mg), *trans*-9-decalinyl hydroperoxide (500 mg), and deaerated benzene (100 mL) was heated under reflux for 2 h. GLC analysis of the mixture revealed that the major product (75%) was 2-(3-butenyl)cyclohexanone (**10**), which was isolated by evaporation of the solvent and chromatography of the residue on silica gel; IR (film) 1705 cm^{-1}; ^1H NMR δ 1.0–2.5 (complex m, 13 H), 4.8–5.0 (m, 2 H, $=CH_2$), 5.4–5.8 (m, 1 H, CH=), identical with an authentic sample.

B. Repetition of the above experiment with cupric octanoate catalyst gave a similar result.

C. *trans*-9-Decalinyl hydroperoxide (170 mg) was slowly added to a vigorously stirred mixture of ferrous sulfate (1.40 g), water (3 mL), concentrated sulfuric acid (0.2 mL), and ethanol (1 mL). After being stirred for a further 30 min, the reaction mixture was diluted with water and extracted with dichloromethane. Evaporation of the extract and separation of the residue by HPLC gave 2-butylcyclohexanone[6] (100 mg, 65%); IR (CCl_4) 1715 cm^{-1}.

D. A deaerated solution of cupric acetate (125 mg, 0.63 mmol), and the peroxide (85 mg, 0.50 mmol) in acetic acid (2.0 mL) and methanol (2.5 mL) was stirred at 0 °C while a solution of ferrous sulfate (120 mg, 0.50 mmol) in 1 M H_2SO_4 (0.5 mL) was added during 20 min. The mixture was stirred at 0 °C for a further 20 min, water and ether were then added, and the ether layer was separated, washed with $NaHCO_3$ solution, dried, and evaporated to afford 2-(3-butenyl)cyclohexanone (77 mg, quantitative).

Reduction of 6-Bromocyclodecanone (4, X = Br) with Tributylstannane. A. A solution of 6-bromocyclodecanone (34 mg, 0.146 mmol), tributylstannane (75 mg, 0.258 mmol), and azodiisobutyronitrile (ca. 1 mg) in benzene (0.2 mL) was degassed, sealed in an ampoule, and heated at 60 °C for 15 h. GLC analysis then showed the presence of *cis*-9-decalinol (75%), *trans*-9-decalinol (20%), and cyclodecanone (4%), each of which was isolated by HPLC and its identity confirmed by comparison with authentic compounds.

B. GLC analysis of the mixture obtained when a solution of 6-bromocyclodecanone (174 mg, 0.75 mmol), tributylstannane (436 mg, 1.50 mmol), and AIBN (10 mg) in benzene (30 mL) was heated at 60 °C for 3 days showed the presence of *cis*-9-decalinol, *trans*-9-decalinol, and 2-butylcyclohexanone, in the ratio 1:1:2.

Reduction of 2-(4-Bromobutyl)cyclohexanone (6, X = Br) with Tributylstannane. Treatment of **6** (X = Br) (28 mg, 0.12 mmol) with tributylstannane (35 mg, 0.12 mmol) in benzene (5 mL) at 60 °C for 15 h gave 2-butylcyclohexanone, detected by GLC and identified, after isolation by HPLC and comparison with an authentic specimen, and a small amount (<10%) of unidentified material.

Bicyclo[5.3.0]decan-2-one (7). 6-Bromocyclodecanone (126 mg) was heated under reflux with KOH (96 mg) in ethanol (3 mL) for 1 h. The mixture was then diluted with water and extracted with ether to give bicyclo[5.3.0]decan-2-one (70 mg, 85%), which gave a 2,4-DNP derivative, mp 218–219 °C, identical with that of the authentic trans ketone.

Registry No. *cis*-1 (X = H), 3574-58-1; *trans*-1 (X = H), 1654-87-1; *cis*-1 (X = Br), 87307-09-3; *trans*-1 (X = Br), 87307-10-6; *cis*-1 (X = NO), 87307-11-7; *trans*-1 (X = NO), 87307-12-8; *trans*-1 (X = OH), 26581-25-9; *cis*-**2**, 87307-13-9; *trans*-**2**, 87307-14-0; **4** (X = Br), 87307-15-1; **6** (X = Br), 51953-08-3; **7**, 56029-64-2; **7** 2,4-DNP, 87307-16-2; **10**, 16178-83-9; **11**, 87307-17-3; **12**, 87307-18-4; **13**, 87307-19-5; cupric acetylacetonate, 46369-53-3; cupric octanoate, 3890-89-9; cupric acetate, 142-71-2; tributylstannane, 688-73-3.