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RING CLOSURE OF THE 6-METHYLENECYCLODECYL RADICAL

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Abstract: Treatment of the dithiocarbonate, **10a**, derived from 6-methylenecyclodecanol, with tributylstannane affords a mixture of the *cis*- and *trans*- isomers of 9-methyldecahydronaphthalene, in which the former predominates, but no methylenecyclodecane. The reaction involves the extremely rapid, stereoselective transannular cyclisation of the 6-methylenecyclodecyl radical (**2b**). Generation of **2b** by thermolysis of the *tert*-butyl perester, **12b**, in the presence of 1,1,3,3-tetramethylisoindolinyl-2-oxyl (**T•**.) gives both cyclised (**15, 16**) and uncyclised (**14**) products. The usual treatment of the data gives $k_c \approx 3 \times 10^{10}$ s^{-1} at 80°C, where k_c is the rate constant for cyclisation of **2b**.

Reduction of 6-bromocyclodecanone (**1a**, Y=Br) with tributylstannane has been shown to give mainly *cis*- and *trans*-9-decalinol (**6a, 7a**) with the former predominating.[1] The mechanism (Scheme 1) involves the intermediacy of the 6-oxocyclodecyl radical (**2a**) which undergoes regiospecific, stereoselective ring closure to afford the *cis*-9-decalinoxy radical (**3a**) and its *trans*-isomer (**4a**).

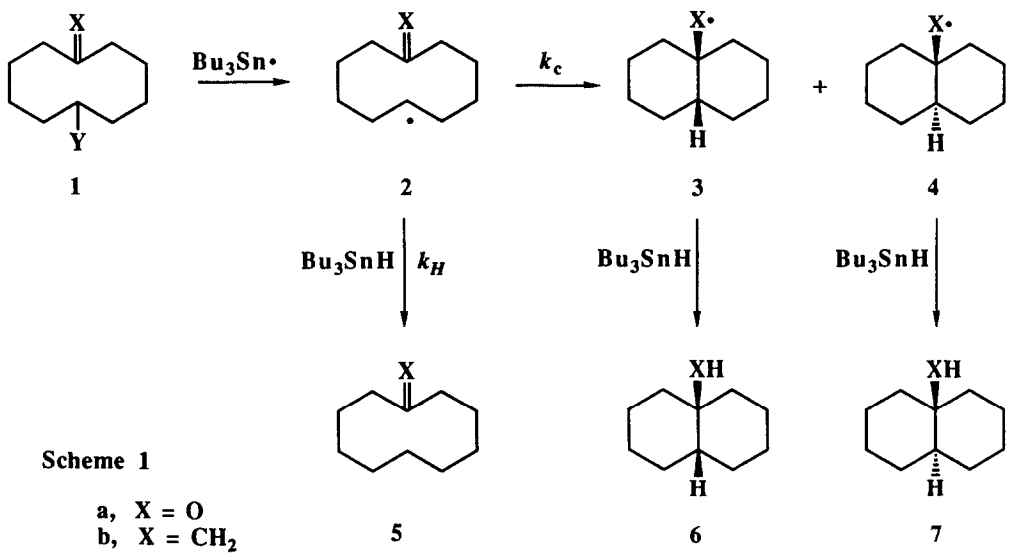
The preferential formation of the *cis*-radical (**3a**) does not conform to the pattern of behaviour usually exhibited by radical cyclisations.[2,3] Examination of models of possible transition structures reveals no obvious steric reason why that on the pathway to the *cis*-radical (**3a**) should be favoured. Nor should the formation of the *cis*-radical be thermodynamically preferred. Experimental[4,5] and theoretical[6] studies indicate that *trans*-9-methyldecalin (**7b**) is more stable than its *cis*-isomer (**6b**). By analogy the *trans*-radical (**4a**) is expected to be more thermodynamically stable than the *cis*-radical (**3a**).

Another noteworthy feature of the ring closure of the 6-oxocyclodecyl radical (**2a**) is its rapidity. Although accurate rate constants have not been determined, the relative yields of cyclised and uncyclised products from the reaction of **1a** (Y=Br) with 1.3 M tributylstannane indicate that $k_c \approx 1 \times 10^8$ s^{-1} at 60°C.[1] This value is more than three orders of magnitude greater than that for ring closure of analogous acyclic species.[7]

With the aim of identifying the factors responsible for the unexpected stereoselectivity of ring closure of the 6-oxocyclodecyl radical (**2a**) and its high rate constant, we have now examined the behaviour of its carbon analogue, the 6-methylenecyclodecyl radical (**2b**). Suitable methods for the generation of **2b** have been developed, and the stereochemistry and kinetics of ring closure, both relative and absolute, have been determined.

Results and Discussion

Since the reaction of alkyl halides with tributylstannane involves the intermediacy of the corresponding carbon-centred radicals,[8] 1-bromo-6-methylenecyclodecane (**1b**, Y=Br) should be a suitable precursor for **2b**. However, all attempts to prepare **1b** (Y=Br) were unsuccessful. 6-Hydroxycyclodecanone (**1a**, Y=OH), which was readily obtained in two steps from decalin hydroperoxide,[9] was converted into the methylene compound (**8**) by a Wittig reaction in dimethyl sulfoxide.[10] However treatment of **8** with *N*-bromosuccinimide/triphenylphosphine[11] failed to give the required bromide (**1b**, Y=Br); nor was the corresponding iodide (**1b**, Y=I) obtained from treatment of **8** with sodium iodide/chlorotrimethysilane.[12] Direct methylenation of 6-bromocyclodecanone (**1a**, Y=Br) by Lombardo's method[13] was also unsuccessful. In each case the ^{1}H NMR spectrum of the crude product revealed the absence of vinyl protons. The most plausible explanation is that the halides (**1b**, Y=Br or I), once formed, undergo rapid rearrangement to the bicyclo[4.4.1]undecane species (**9b**, **9c**). It is known that the alcohol (**8**) readily rearranges to **9a**, and that its tosylate behaves similarly.[10,14]

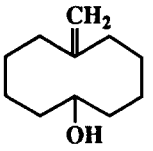


Scheme 1

a, X = O
b, X = CH_2

In view of the unavailability of suitable halides we decided to examine the feasibility of generating radical **2b** from dithiocarbonates and similar species. It is well established that Barton deoxygenation of secondary alcohols by treatment of their dithio- or thiono-carbonates with tributylstannane involves the intermediacy of the corresponding alkyl radicals, generated by addition of the tributylstannyl radical to the thiono group.[15-17] The chain is then propagated in the usual way by hydrogen-atom transfer from stannane to the alkyl radical. Although the method is generally efficient, dithiocarbonates sometimes give unreduced byproducts.[15,18]

As possible precursors for the radical **2b**, *O*-(6- methylenecyclodecyl)-*S*-phenyldithio-carbonate (**10a**) and *O*-(6-methylenecyclodecyl)-*O*- phenylthionocarbonate (**10c**) were prepared by treatment of the alcohol, **8**, with the appropriate chloride in pyridine/dichloromethane. The *S*-methyl dithiocarbonate, **10b**, was obtained from **8** by the usual procedure.[16] Authentic samples of the expected cyclisation products, **6b** and **7b**, were respectively prepared by reduction of *cis*-9-(bromomethyl)decalin with lithium aluminium hydride, and by treatment of decalin with tetramethylsilane-aluminium chloride.[19]



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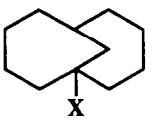
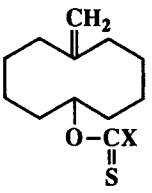
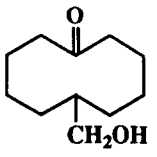


9 a, X = OH
b, X = Br
c, X = I



10 a, X = PhS
b, X = MeS
c, X = PhO



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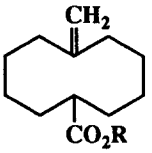
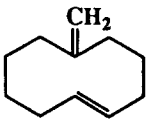


12 a, R = H
b, R = OBu^t



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During the course of this work (see below) it became necessary to generate the radical **2b** by thermolysis of a suitable precursor; the *tert*-butyl perester, **12b**, was chosen for this purpose. Hydroboration/oxidation of **8**, followed by selective Swern oxidation of the secondary alcohol gave the keto-alcohol, **11**, which was converted into the acid, **12a**, by a Wittig reaction followed by treatment with Jones' reagent. The *tert*-butyl perester, **12b**, was readily prepared from **12a** in the usual way.[20]

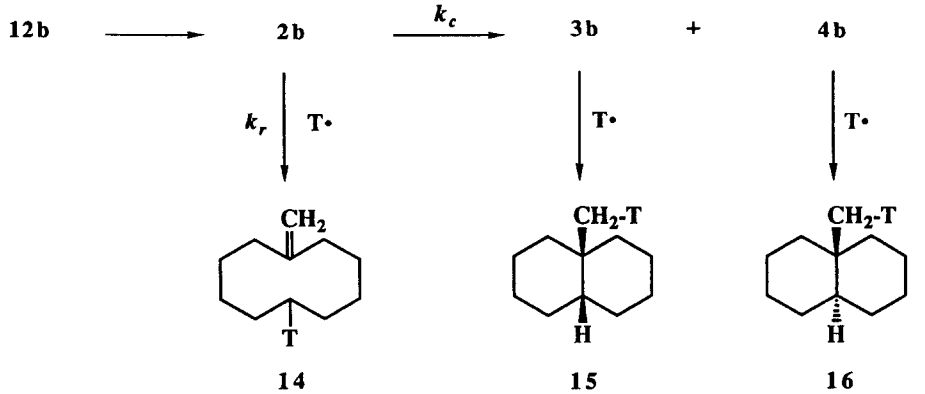
Each of the thiocarbonates, **10a**, **10b** and **10c**, was heated in benzene at 80°C with tributylstannane in large molar excess and a small amount of azobisisobutyronitrile (AIBN) as initiator, and the product mixture was analysed by GC after addition of durene as internal standard. In each case *cis*- and *trans*-9-methyldecalin, **6b** and **7b**, were detected, but only in the case of the dithiocarbonate **10a** were they the sole hydrocarbon products. The other two precursors, **10b** and **10c**, also gave a compound tentatively identified as the diene, **13**, presumably formed by direct thermal elimination, together with other unidentified products. In no case could the uncyclised reduction product, **5b**, be detected. Since only **10a** gave quantitative yields of THE products expected on the basis of Scheme 1, further kinetic studies were confined to this precursor.

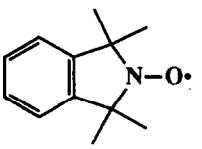
From all of the reactions, *cis*-9-methyldecalin (**6b**) was the major product. Clearly, the radical **2b**, like its oxo analogue, **2a**, undergoes stereoselective ring closure to give mainly the *cis* radical, **3b**. As expected, the *cis*/*trans* ratio was temperature dependent ranging from 3.5 at 60°C to 2.3 at 122°C. Since the ratio of products

6b/7b should reflect the ratio k_c^{cis}/k_c^{trans} of the two cyclisation rate constants, it should be possible to obtain a temperature dependence in the usual way. Linear regression of the data for k_c^{cis}/k_c^{trans} in the Experimental section against 1/T gives log $(k_c^{cis}/k_c^{trans}) = (-0.63 \pm 0.06) + (1.81 \pm 0.12)/\theta$, where $\theta = 2.3RT$ kcal/mole.

Rate constants for rearrangements of radicals generated by the stannane method can usually be deduced from the relative yields of rearranged and unrearranged products, since application of steady-state kinetics to the reactions of Scheme 1 when the stannane is in large excess affords an integrated rate equation: $k_c/k_H = [Bu_3SnH]_m([6] + [7])/[5]$, where k_c is the rate constant for rearrangement, k_H is that for hydrogen atom transfer from stannane to unrearranged radical, $[Bu_3SnH]_m$ is the mean concentration throughout the reaction, and the other terms represent final concentrations of products. Representative values of k_H are available; in this case the value for isopropyl radical ($k_H \approx 6.3 \times 10^6$ M^{-1} s^{-1} at 80°C)[21] is appropriate. However, no unrearranged product could be detected even at the highest possible stannane concentration (*ca* 3M). Since the analytical method was capable of detecting **5b** if it comprised 1% or greater of total product, it can be deduced that k_c, the rate constant for ring closure of **2b**, has a lower limit of about 8×10^8 s^{-1} at 80°C.

Earlier work[20,22] has established the utility of nitroxyl coupling for following the kinetics of very fast radical reactions. Essentially, the method employs the coupling of radicals with the nitroxyl radical, 1,1,3,3,-tetramethylisoindolinyl-2-oxyl (**T•**), to give hydroxylamines, e.g. **14**, as a kinetic yardstick against which the rates of competing processes can be measured. Since the reaction of **2b** with stannane is too slow to compete detectably with its cyclisation we decided to apply the nitroxyl coupling method.



Scheme 2 T• = 

Thermolysis of **12b** at 80°C in cyclohexane containing an excess of the nitroxyl radical, **T•**, gave pure samples of the *cis*- and *trans*-cyclised products, **15** and **16** (Scheme 2), identified by comparison with authentic specimens prepared from *cis*- and *trans*-9-decahydronaphthylacetic acid[23] via their *tert*-butyl peresters. The

unrearranged product, **14**, could not be separated from **16** by HPLC, but could be detected and estimated by NMR which revealed a characteristic resonance for the vinyl protons at δ 4.96. Consequently, product mixtures could be fully analysed by a combination of HPLC and NMR. Thus, heating of a solution of **T•** (0.30 M) and **12b** (0.10 M) at 80°C gave **15**, **16** and **14** in the ratio of yields 2.7 : 1.0 : 0.082, while at 123°C the same products were formed in the ratio 2.1 : 1.0 : 0.041. When the initial reactant concentrations were raised to $[T•]_i$ = 0.60 M and $[12b]_i$ = 0.20 the ratio of yields of **15**, **16** and **14** at 80°C was 2.8 : 1.0 : 0.18. In each case the total yield of products was in the range 60-70%.

Steady state treatment of the reactions of Scheme 2 gives k_c/k_T = [T•]([15] + [16])/[14], where [T•] is the mean concentration of T• throughout the experiment, and the other concentration terms represent the final concentrations of products. Substitution of the above results into this expression gives $k_c/k_T \approx 11$ M at 80°C and ~ 19 M at 123°C. Substitution of the probable values of k_T (1.4×10^9 M^{-1} s^{-1} at 80°C and 1.6×10^9 M^{-1} s^{-1} at 123°C)[20] gives $k_c^{cis} \approx 1.1 \times 10^{10}$ s^{-1} at 80°C and 2.0×10^{10} s^{-1} at 123°C, and $k_c^{trans} \approx 0.4 \times 10^{10}$ s^{-1} at 80°C and 1×10^{10} s^{-1} at 123°C. The very approximate Arrhenius parameters derived from these data, *viz* (log $A^{cis}/s^{-1}) \approx 12.4$, $E^{cis} \approx$ 3.8 kcal/mole, and log $(A^{trans}/s^{-1}) \approx$ 13.0, $E^{trans} \approx$ 5.6 kcal/mole, are consistent with the temperature dependence of the more accurate values of the *cis/trans* ratios obtained by the stannane method as described above.

Although these data are subject to substantial error, they clearly indicate that the 5-methylenecyclodecyl radical (**2b**), like the corresponding oxo radical (**2a**),[1] undergoes ring closure much more rapidly than simple acyclic species (*cf.* 5-hexenyl radical, $k_c = 1.4 \times 10^6$ s^{-1} at 80°C).[21] Indeed the cyclisation of **2b** appears to be one of the fastest radical rearrangements yet recorded.[22]

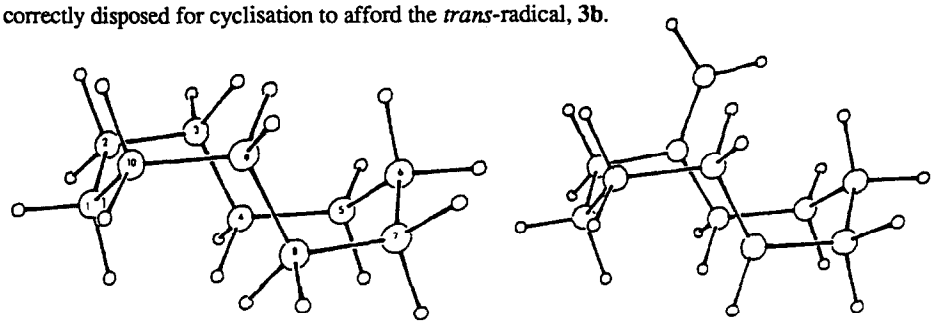
A major contribution to the high rate of ring closure of **2b** comes from the relatively large value of log *A* which is well above the range typically found for cyclisation of acyclic radicals (10.0 - 10.4).[2,20,21] Formation of cyclic transition structures from the latter species involves a considerable loss of rotational freedom. By contrast, transannular cyclisation of cyclic radicals such as **2b**, in which both the radical centre and the double bond are already rotationally constrained, imposes a relatively small loss of internal freedom.

Although the relatively high rates of cyclisation of radicals **2a** and **2b** can thus be rationalised, there is no equally plausible explanation available for the observed preference for formation of the *cis*-fused products. It is interesting to note, however, that the preference for the formation of the *cis*-radical, **3b**, is a consequence of the lower activation energy for its formation (see above). Indeed, the temperature dependence of the *cis/trans* ratio shows that formation of the *trans*-radical (**4b**) is entropically preferred, the balance of factors favouring the *cis*-radical (**3b**) at the temperatures used in this study.

In view of the success of the MM2/MNDO method for determining the strain energies of radical transition structures,[3] similar calculations were performed on a number of low energy conformations of possible transition structures leading to **3b** and **4b** in the hope that they would provide an explanation for the formation of the former. However, the two conformers of lowest energy of the transition structure for cyclisation were very similar in general shape to *cis*- and *trans*-9-methyldecalin. As expected on the basis of the thermodynamic

stabilities of the decalins, the strain energy of the transition structure for *trans*-cyclisation was found to be 1.4 kcal/mole less than that for *cis*-cyclisation.

We turned next to a consideration of the preferred conformation of the 6-methylenecyclodecyl radical, **2b**. NMR,[24] crystal structure,[25] and strain energy calculations[26,27] all indicate the "diamond lattice" boat-chair-boat (BCB) conformation of cyclodecane to be the form of lowest energy. Molecular mechanics calculations suggest that cyclodecyl radical, like cyclodecanone, also prefers the BCB form with the radical centre at C-3 since this lowers the number of unfavourable transannular interactions.[28] By analogy, the conformation of lowest energy for the 6-methylenecyclodecyl radical (**2b**) should be the BCB form (**17**). Clearly, this conformation is correctly disposed for cyclisation to afford the *trans*-radical, **3b**.



cyclodecane BCB **6-methylenecyclodecyl radical BCB-3 (17)**

Anet and coworkers[24] have determined the rate constants for conformational change in cyclodecanone to be about 2 x 10^5 s^{-1} at 80°C. The rate constant for interconversion of the conformers of **2b** is likely to be in the range 10^5 - 10^6 s^{-1}, that is some 4-5 orders of magnitude less than the cyclisation rate constant. It seemed possible, therefore, that the preferred mode of cyclisation might reflect the conformational preference of the radical precursors. 1-Iodo-6-methylenecyclodecane was chosen as a convenient heavy atom model for such precursors, and possible conformations were analysed by molecular mechanics calculations. It was found that the BCB-3 and TCCC (crown) forms, each of which should lead to *trans*-cyclisation, were of lower energy than that, the CBC-3 form, which leads to *cis*-cyclisation. The calculated energy difference between BCB-3 and CBC-3, the least and most energetic forms, was 3.7 kcal/mole (Fig. 3)

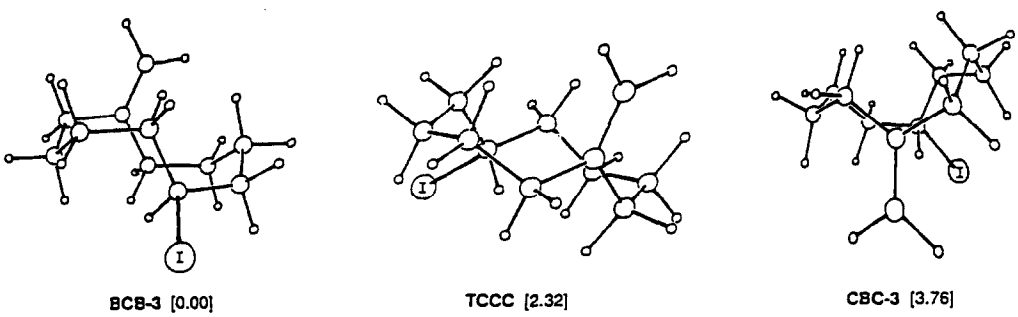


Figure 3. Low energy conformations of 1-iodo-6-methylenecyclodecane and associated strain energies [kcal/mol]

It appears, therefore, that the stereoselectivity of cyclisation of the 6- methylenecyclodecyl radical, unlike the majority of such reactions, is not amenable to prediction by the MM2/MNDO method. Perhaps the system is too complex: Allinger[27] has suggested that there are too many conformations available in systems such as these to allow an effective and valid study. On the other hand, it may be that this is an example of a radical ring closure for which factors other than steric are dominant. The other groups of radicals the cyclisation behaviour of which cannot yet be satisfactorily rationalised are the 1-substituted-ω–alkenyl radicals such as 1-methyl-6-heptenyl radical.[2,29] It is intriguing to note that the 6-methylenecyclodecyl radical belongs to this class.

Experimental

General. Details of instrumentation, solvents, reagents, general experimental methods chromatographic procedures, etc., have been given in full in recent publications.[7,20]

Materials. 6-Methylenecyclodecanol (**8**) was prepared from 6-hydroxycyclodecanone[9] as previously described.[10] Methylenecyclodecane (**5b**), similarly prepared by cyclodecanone, had ν_{max} 3070, 2960, 1640 cm^{-1}, δ ($CDCl_3$) 5.85 (s, 2H), 2.20 (m, 4H), 1.3-1.8 (m, 14H). 1,1,3,3-Tetramethylisoindolinyl-2-oxyl (**T•**), prepared in three steps from N-benzylphthalimide as previously described,[30] formed yellow plates, mp 128°C.

***O*-(6-Methylenecyclodecyl)-*S*-phenyl Dithiocarbonate (10a).** (Phenylthio)thiocarbonyl chloride (245 mg, 1.30 mmol) was added to a deoxygenated solution of 6-methylenecyclodecanol (200 mg, 1.19 mmol) and pyridine (350 mg, 4.4 mmol) in dry dichloromethane (7.0 mL), and the mixture was heated under reflux for 48 h. After being cooled the mixture was washed with 10% aqueous H_2SO_4, aqueous $NaHCO_3$, and brine, dried, and evaporated in vacuo. The residue was purified by preparative TLC (10:1 hexane-CH_2Cl_2) to give the required dithiocarbonate (**10a**) as a pale yellow oil (125 mg, 33%) which solidified on standing, mp 41-42.5°C: IR 1635, 1470, 1440, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (s, 5H), 5.81 (m, 1H), 4.79 (s, 2H), 1.20-2.31 (m, 16H). Anal. Calcd for $C_{18}H_{24}OS_2$: C, 67.46; H, 7.55. Found: C, 67.64, H, 7.73%.

***O*-(6-Methylenecyclodecyl)-*O*-phenyl Thionocarbonate (10c).** Treatment of 6-methylenecyclodecanol (200 mg) with phenyl chlorothionocarbonate (225 mg) as described for **10a**, with stirring at room temperature for 1 h gave the required thionocarbonate (**10c**) which was obtained as a pale green oil (215 mg, 62%) after purification by preparative TLC (10:1 hexane-$CHCl_2$): ^1H NMR ($CDCl_3$) δ 7.01-7.54 (m, 5H), 5.63 (m, 1H), 4.85 (s, 2H), 1.22-2.23 (m, 16H).

***O*-(6-Methylenecyclodecyl)-*S*-methyl Dithiocarbonate (10b).** Sodium hydride (50 mg, 208 mmol) and imidazole (ca 2 mg) were added to a deoxygenated solution of 6-methylenecyclodecanol (200 mg, 1.19 mmol) in dry tetrahydrofuran, and the mixture was boiled under reflux under nitrogen for 3.5 h, after which time carbon disulfide (0.4 mL, 6.6 mmol) was added. After 30 min, methyl iodide (0.4 ml, 6.5 mmol) was added, and heating was continued for a further 30 min. The mixture was then cooled, diluted with water, and extracted with CH_2Cl_2. The combined organic phases were washed with aqueous $NaHCO_3$, dilute HCl, and brine, dried, and evaporated in vacuo to afford the required dithiocarbonate (**10b**) which was obtained after

purification by preparative TLC (CH_2Cl_2) as a yellow oil (165 mg, 54%): IR 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (m, 1H), 4.87 (s, 2H), 2.48 (s, 3H), 1.22-2.43 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 215.5, 148.2, 111.0, 83.9, 33.9, 30.0, 22.0, 18.7.

Attempted distillation of crude **10b** (1.65 g) gave a mixture of dimethyl trithiocarbonate and an olefin which was isolated by flash chromatography and purified by bulb to bulb distillation (Kuegelrohr) at 100°C/mmHg to give a colourless oil (30 mg, 34%), tentatively identified as 6-methylenecyclodec-1-ene (**13**): IR 1635, 2960, 3320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.39 (m, 2H), 4.81 (s, 2H), 1.05-2.28 (m, 14H); Anal. Calcd for $C_{11}H_{18}$: C, 87.93, H, 12.07. Found: C, 87.7; H, 12.25.

9-Methyl-*cis*-decahydronaphthalene (6b). A solution (0.1 M) of lithium aluminium hydride (12.0 ml, 12.0 mmol) in tetrahydrofuran was added to 9-(bromomethyl)-*cis*-decahydronaphthalene (1.08 g, 4.7 mmol) under nitrogen in a quartz round bottom flask. Di-*tert*-butyl peroxide (5.0 ml) was added, and the mixture was stirred while being irradiated with a 250 W mercury lamp. After 2 h, analysis by GC showed that all of the bromo compound had been consumed. Water was then continuously added, the mixture was extracted with pentane, and the organic layer was evaporated to afford crude 9-methyl-*cis*-decahydronaphthalene (760 mg). A pure sample, obtained by preparative TLC (light petroleum, bp 30-40°C), had IR, ^1H NMR, and ^{13}C NMR spectra identical with those previously reported.[31,32]

9-Methyl-*trans*-decahydronaphthalene (7b). Tetramethylsilane (10 mL) was added to a solution of tetrahydronaphthalene (1.0g, 7.3 mmol) in CH_2Cl_2 (20 mL), followed by aluminium chloride (3.0 g, 22 mmol), and the mixture was heated for 6 h under reflux. A further portion (10 mL) of tetramethylsilane was then added, and the mixture was set aside at room temperature for 15 h, after which time GC analysis showed it to contain a mixture of **6b** and **7b** (47%). The reaction mixture was then poured into water (20 mL) and extracted with CH_2Cl_2. Evaporation of the organic layer gave a yellow oil, which was subjected to preparative GC to give a sample of pure 9-methyl-*trans*-decahydronaphthalene (**7b**) with ^1H NMR and ^{13}C NMR identical with those reported in the literature.[33]

Methylenecyclodecane (5b). Sodium hydride (180 mg, 7.5 mmol) was added to dry DMSO (5 mL), and the mixture was stirred under nitrogen at 70°C until the evolution of hydrogen had ceased (ca 45 min). Methyltriphenylphosphonium iodide (2.0 g, 4.95 mmol) in dry DMSO (15 mL) was then added, and the mixture was stirred at 70°C for 15 min. Cyclodecanone (400 mg, 2.6 mmol) in dry DMSO (5 mL) was added, and the mixture was stirred for a further 2 h, after which time it was cooled, poured into water, and acidified with 15% aqueous H_2SO_4. Extraction with pentane, and evaporation of the solvent afforded a pale yellow oil, identified as **5b** by its IR, ^1H NMR, and ^{13}C NMR spectra, which were identical with those previously recorded.[34]

***tert*-Butyl 6-Methylenecyclodecaneperoxycarboxylate (12b).** A suspension of oil-free sodium hydride (440 mg, 18 mmol) in dry DMSO (20 mL) was stirred at 70°C until gas evolution ceased (ca 45 min). Methyltriphenylphosphonium iodide (7.5 g, 20 mmol) in DMSO (25 mL) was added, followed, after 10 min, by 6-(hydroxymethyl)cyclodecanone (**11**, 1.6 g, 9.0 mmol) in DMSO (25 mL). After 2 h at 70-75°C, the reaction mixture was diluted with water (100 mL) and extracted with pentane. The organic layer was evaporated and the residue chromatographed on silica to afford 6-(hydroxymethyl)methylenecyclodecane as a viscous colourless oil (1.28 g, 78%): ^1H NMR (CCl_4) δ 4.75 (s, 2H), 3.35 (d, 2H), 2.1-2.5 (m, 5H), 1.3-2.0 (m, 13H).

Jones' Reagent[35] was added dropwise to a solution of this alcohol (180 mg, 10 mmol) until the brown colour persisted for 10 min. The mixture was then filtered through Celite, and evaporated, and the residue was purified by Kuegelrohr distillation to afford 6-methylenecyclodecanecarboxylic acid (180 mg, 92%) which crystallised from pentane as plates, mp. 65-67°C: IR 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (s, 2H), 2.61 (m, 1H), 2.15 (m, 4H), 1.4-1.8 (m, 13H). The acid was converted via its acid chloride by procedures previously described, into the perester **12b** (61%): IR 1778, 1794 cm^{-1}; ^1H NMR δ 4.86 (m, 1H), 2.61 (m, 1H), 2.15 (m, 4H), 1.4-1.8 (m, 13H), 1.31 (s, 9H).

2-(*cis*-9-Decahydronaphthyl)methoxy-1,1,3,3-tetramethylisoindoline (15). *cis*-9- Decahydronaphthaleneacetic acid[23] (100 mg, 0.51 mmol) was converted via its acid chloride as previously described,[20] into its *tert*-butyl perester (76 mg, 56%): IR (CCl_4) 1772, 1790 cm-1; ^1H NMR δ 2.71 (s, 2H), 1.05-1.9 (m, 17H), 1.10 (s, 9H). Heating of a solution of this perester and 1,1,3,3-tetramethylisoinolinyloxyl in benzene under reflux gave the trapped product 15 (71%): ^1H NMR ($CDCl_3$) δ 7.14 (m, 2H), 7.05 (m, 2H), 3.93 (s, 2H), 2.18 (m, 4H), 1.53-1.95 (m, 18H), 1.21 (s, 6H).

2-(*trans*-9-Decahydronaphthyl)methoxy-1,1,3,3-tetramethylisoindoline (16). *trans*-9-Decahydronaphthaleneacetic acid[23] (100 mg, 0.51 mmol) was similarly converted into its *tert*-butyl perester (71 mg, 52%): IR (CCl_4) 1784, 1768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (s, 2H), 1.1-1.8 (m, 17H), 1.08 (s, 9H). When heated under reflux in benzene with the nitroxyl (**T•**) it gave the trapped product (**16**): ^1H NMR ($CDCl_3$) δ 7.14 (m, 2H), 7.05 (m, 2H), 3.70 (s, 2H), 2.18 (m, 4H), 1.50-1.90 (m, 18H), 1.23 (brs, 6H).

Reaction of Tributylstannane with Thiocarbonates 10a, 10b and 10c. An aliquot (100 mL) of a standard solution (0.1 M) of tributylstannane in degassed benzene was placed in a small pyrex tube, the required precursor (~ 0.001 mmol), and a small amount (~ 0.01 mg) of azo-bis-isobutyronitrile was added, and the mixture was further degassed by the usual freeze-thaw technique, before being sealed under vacuum. After being heated at the required temperature for 12-16 h, the mixture was analysed by GC on a capillary column (SGE-25QC2/BP1). The *cis/trans* isomer ratios for 9-methyldecalin obtained from **10b** at various temperatures were 60°C, 3.5; 71°C, 3.3; 80°C, 3.0; 91°C, 2.8; 122°C, 2.3.

Thermolysis of 12b in the Presence of T•. Aliquots of a stock solution of the nitroxyl radical, T• (0.30 mmol/mL), and the perester, **12b** (0.10 mmol/mL) in cyclohexane were placed in 1 mL Pyrex ampoules, degassed by the free-thaw techniques, and sealed under vacuum They were then heated at 80°C for 4 h, cooled, and analysed by reversed phase HPLC (H_2O/MeOH).[20] UV detection showed two peaks, one corresponding to the *cis*-adduct (**15**) the other to a mixture of the *trans*-adduct (**16**) and the uncyclised adduct (**14**), the relative amounts of which were determined by ^1H NMR spectroscopy. The total yield in this and other experiments was in the range 60-70%, and the ratio of 15:16:14 was 2.7 : 1.0:0 . 082. The same stock solution of reactants when heated at 123°C for 18 min gave the ratio of yields **15:16:14** as 2.1 : 1.0 : 0.041. When the reaction at 80°C was carried out with [T•] = 0.60 M and [**12b**] = 0.20 M the ratio 15:16:14 was 2.8 : 1.0 : 0.18.

References

(1) Beckwith, A.L.J.; Kazlauskas, R.; Syner-Lyons, M.R. *J. Org. Chem.* **1983**, *48*, 4718.
(2) Beckwith, A.L.J. *Tetrahedron* **1981**, *37*, 3073.

(3) Beckwith, A.L.J.; Schiesser, C.H. *Tetrahedron* **1985**, *41*, 3925.
(4) Dauben, W.G.; Rohr, O.; Labrauf, A.; Rossini, F.D. *J. Phys. Chem.* **1960**, *64*, 283.
(5) Allinger, N.L.; Coke, J.L. *J. Org. Chem.* **1961**, *26*, 2096.
(6) Allinger, N.L.; Miller, M.A.; VanCatledge, F.A.; Hirsch, J.A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.
(7) Beckwith, AL.J.; O'Shea, D.M.; Westwood, S.W. *J. Am. Chem. Soc.* **1988**, *110*, 2565.
(8) Kuivila, H.G. *Acc. Chem. Res.* 1968, **1**, 299; Carlsson, D.J.; Ingold, K.U. *J. Am. Chem. Soc.* **1968**, **90**, 1055.
(9) Cope, A.C.; Holzman, G. *J. Am Chem. Soc.* **1950**, *72*, 3062.
(10) Becker, K.B.; Chappuis, J.L. *Helv. Chim. Acta.* **1979**, *62*, 34.
(11) Coe, D.G.; Landauer, S.R.; Rydon, H.N. *J. Chem. Soc.*, **1954**, 2281.
(12) Olah, G.A.; Narang, S.C.; Gupta, B.G.B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.
(13) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293.
(14) Westman, T.L.; Stevens, R.D. *J. Chem. Soc., Chem. Commun.* **1965**, 459.
(15) Barton, D.H.R.; McCombie, S.W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
(16) Barton, D.H.R.; Crich, D.; Löbberding, A.; Zard, S.Z. *Tetrahedron* **1986**, *42*, 2329.
(17) For a recent review see Crich, D.; Quintero, L. *Chem Rev.* **1989**, *89*, 1413.
(18) Robins, M.J.; Wilson, J.S.; Hansske F. *J. Am. Chem. Soc.* **1983**, *105*, 4059; Acton, E.M.; Goerner, R.N.; Uh, H.S.; Ryan, K.J.; Henry, D.W.; Cass, C.E.; LePage, G.A. *J. Med. Chem.* **1979**, *22*, 518. Brimacombe, J.S.; Mengech, A.S.; Saeed, M.S. *Cabohydr. Res.* **1979**, *75*, C5. Hayashi, T.; Iwaoka, T.; Takeda, N.; Ohki, E. *Chem. Pharm. Bull.* **1978**, *26*, 1786.
(19) Kursanov, D.N.; Bolestova, G.I.; Kataev, V.A.; Parnes, Z.N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, *28*, 1919.
(20) Beckwith, A.L.J.; Bowry, V.W.; Moad, G. *J Org. Chem.* **1988**, *53*, 1632.
(21) Chatgilialoglu, C.; Ingold, K.U.; Scaiano, J.C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
(22) Bowry, V.W.; Lusztyk, J.; Ingold, K.U. *J. Am. Chem. Soc.* **1989**, *111*, 1927; Bowry, V.; Lusztyk, J.; Ingold, K.U. *Pure Appl. Chem.* **1989**, *62*, 213
(23) Mander, L.N.; Prager, R.H.; Turner, J.V. *Aust. J. Chem.*, **1974**, *27*, 2645.
(24) Anet, F.A.L.; Jacques, M.St.; Henrichs, P.M.; Cheng, A.K.; Krane, J.; Wong, L. *Tetrahedron* **1974**, *30*, 1629.
(25) Dunitz, J.D. *Pure Appl. Chem.* **1971**, *25*, 495.
(26) Allinger, N.L.; Tribble, M.T.; Miller, M.A. *Tetrahedron* **1972**, *28*, 1173; Still, W.C.; Galynker, I. *ibid* **1981**, *37*, 3981.
(27) Burkert U.; Allinger, N.L. *Molecular Mechanics*; American Chemical Society; Washington, D.C., 1982.
(28) Imam, M.R.; Allinger, N.L. *J. Mol. Struct.* **1985**, *126*, 345.
(29) Beckwith, A.L.J.; Blair, I.A.; Phillipou, G. Tetrahedron Lett. **1974**, 2251; Burkhard, P.; Roduner, E.; Hochmann, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 773; Lawrence, T. PhD Dissertation, University of Adelaide, **1979**.
(30) Griffiths, P.G.; Moad, G.; Rizzardo, E.; Solomon, D.H. *Aust. J. Chem.* **1983**, *36*, 397.
(31) Browne, L.M.; Klinck, R.E.; Stothers, J.B. *Org. Mag. Res.* **1979**, *12*, 561.
(32) Dauben, W.G.; Rogan, J.B.; Blanz, E.J.Jr., *J. Am. Chem. Soc.* **1954**, *76*, 6384.
(33) Birnbaum, G.I.; Stoessi, A., Grover, S.H.; Stothers, J.B. *Can. J. Chem.* **1974**, *52*, 993.
(34) Grover, S.H.; Stothers, J.B. *Can. J. Chem.* **1975**, *53*, 589.
(35) Bowden, K.; Heilbron, I.M.; Jones, E.R.H.; Weedon, B.C.L. *J. Chem. Soc.* **1946**, 39