Radical Reactions of Bicyclo[2.1.0]pentane

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The photochemical reactions of bicyclo[2.1.0]pentane with bromine, bromotrichloromethane, t-butyl hypochlorite, di-t-butyl peroxide, and *N*-bromosuccinimide have been investigated. Trichloromethyl, t-butoxyl, and succinimidyl radicals abstract hydrogen from the C_4 ring. The expected bicyclopentyl radicals were not detected and if they are discrete intermediates they must rearrange by fission of the C(1)–C(4) bond common to the two rings to form cyclopent-3-enyl radicals. The e.s.r. spectrum of the latter radicals was obtained. Bromine (and chlorine) atoms may abstract hydrogen, but their major pathway involves attack at the bridgehead carbon atoms in an S_H2 reaction with fission of the C(1)–C(4) bond to give 3-halogenocyclopentyl radicals.

SINCE it was first synthesised by Criegee and Rimmelin [1] in 1957, the chemistry of bicyclo[2.1.0]pentane (1) has received a good deal of attention. Most of the reactivity in cycloaddition and electrophilic processes was found to reside in the C(1)—C(4) bond which is common to both rings, and which, according to microwave measurements,[2] is intermediate in length between that of cyclobutane and cyclopropane. Very few homolytic reactions have been reported. Thermal decomposition gives cyclopentene together with traces of penta-1,4-diene.[3,4] The thermal rearrangement employing the 5,5-dideuteriobicyclopentane showed that the cyclopentene is formed by C(1)–C(4) cleavage with C(5)–H migration.[5] Bicyclopentane reacted with hydrogen peroxide and *N*-bromosuccinimide in diethyl ether to give *cis*- and *trans*-3-bromocyclopentyl hydroperoxides.[6] Boikess and Mackay observed a series of mono- and di-chlorocyclopentanes from the vapour phase chlorination of (1).[7,8] These reactions seem to imply that homolytic attack occurs at C(1) or C(4) with fission of the C(1)–C(4) bond. This conclusion contrasts with the findings from radical halogenation of alkyl-substituted cyclopropanes where attack was always found to occur at the unsubstituted CH_2 group when one was available.[9] By analogy therefore, radical attack on (1) would be expected to occur at C(5) with fission of the C(5)–C(1) or C(5)–C(4) bonds. In this paper we report a study of the reactions of several different radicals with (1) which help to illuminate this situation and map out the homolytic pathways available to (1).

TABLE 1

Products and yields (%)* in photobromination of bicyclopentane in CCl_4 at 0 °C

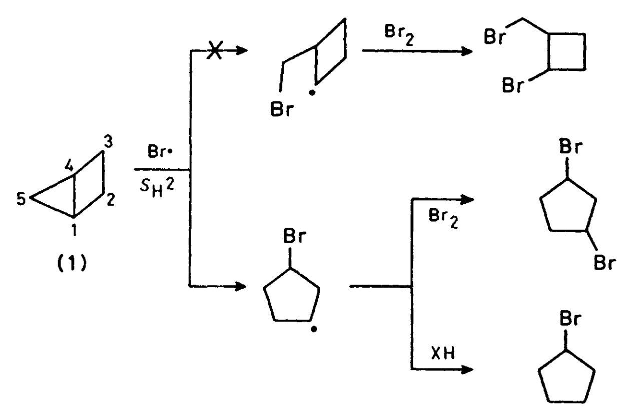
Conditions	Bromo-cyclo-pentane	*trans*-1,2-Dibromo-cyclo-pentane	*cis*-1,3-Dibromo-cyclo-pentane	*trans*-1,3-Dibromo-cyclo-pentane
Excess bicyclo-pentane	13	14	44	28
Excess bromine	4	12	54	30

* Yields are mole % relative to the total products.

RESULTS AND DISCUSSION

Radical Bromination of Bicyclo[2.1.0]*pentane*.—Reaction of (1) with molecular bromine proceeds rapidly and vigorously at 0 °C in CCl_4 without artificial illumination. Products identified were bromocyclopentane, *trans*-1,2-dibromocyclopentane, *cis*- and *trans*-1,3-dibromocyclopentane, and their yields are given in Table 1. No cyclobutyl bromides were found. In the electrophilic bromination of (1) in chloroform, *trans*-1,2-dibromocyclopentane was the main product and no 1,3-dibromocyclopentanes were observed.[10] It seems probable, therefore, that the 10—15% *trans*-1,2-dibromocyclopentane formed here comes from an electrophilic process concurrent with the main radical reaction. Shea and Skell also found *ca*. 10% electrophilic reaction accompanying the radical bromination of alkylcyclopropanes.[9]

Probably the 1,3-dibromides, which are the major products, are formed by a bimolecular radical substitution (S_H2) reaction at C(1) of bicyclopentane (see Scheme 1).



SCHEME 1

The initially-formed 3-bromocyclopentyl radicals react with molecular bromine to give a mixture of the 1,3-dihalides (1.7 *trans*: 1 *cis*). Direct photobromination of bromocyclopentane has been shown to give 1,3-dibromocyclopentanes *via* reaction of 3-bromocyclopentyl radicals with molecular bromine.[11] The observed *trans* : *cis* ratio was 1.5,[11] which is virtually identical with the

ratio quoted above for bicyclopentane, and lends support to the proposed radical mechanism.

Bromocyclopentane is probably formed in part by the 3-bromocyclopentyl radicals abstracting hydrogen from (1) (which is not a particularly good hydrogen atom donor) and in part by reaction of (1) with HBr. Boikess and Mackay showed that (1) reacts with HCl to give chlorocyclopentane (together with cyclopentene) [8] and it seems safe to conclude that HBr reacts in a similar fashion. Certainly there must be some HBr formed by hydrogen abstraction from (1) by bromine atoms since 4-bromocyclopentene was a minor product of the reaction. The reactions yielding bromocyclopentane became less important when the concentration of (1) was kept low by adding it drop by drop to excess bromine (see Table 1). It should be added that the dibromocyclopentanes are not formed *primarily* by the further bromination of bromocyclopentane since direct photobromination of the monobromide gives 1,1-dibromocyclopentane and *trans*-1,2-dibromocyclopentane as the major products.[11] In the bicyclopentane reaction no 1,1-dibromide was formed and the 1,3-dibromides predominated. Moreover, the brominations of bicyclopentane were complete in seconds, whereas bromocycloalkanes take much longer to react.

The absence of cyclobutyl bromides shows that (1) does not undergo S_H2 attack at C(5) by bromine atoms (Scheme 1). *cis*-1,2-Dimethylcyclopropane, which is structurally rather similar to (1), undergoes S_H2 attack *exclusively* at the CH_2 group of the C_3-ring with fission of one of the less substituted bonds.[9] The fact that attack does not occur at the CH_2 site in the cyclopropyl ring of (1) can be accounted for in ring strain terms. Radical attack at C(5) would lead to loss of the cyclopropane ring strain energy (*ca.* 115 kJ mol^{-1}) but retention of the cyclobutane ring strain energy (*ca.* 110 kJ mol^{-1}). S_H2 Attack at C(1) or C(4) on the other hand leads to relief of both the cyclopropane and cyclobutane ring strain energies with only the much smaller cyclopentyl radical strain energy (<27 kJ mol^{-1}) remaining.

TABLE 2

Photochemical reaction (4 h) of CCl_3Br with bicyclopentane at ambient temperature

Product	C_5H_9Br	*trans*-1,2-$Br_2C_5H_8$	*cis*-1,2-$Br_2C_5H_8$		
Yield (%) *	6	18	3		
	C_5H_9Cl	*trans*-1-Br-2-ClC_5H_8	*cis*-1-Br-2-ClC_5H_8		
Yield (%) *	4	12	5		
	C_5H_8	C_5H_7Br	*trans*-1-Br-2-$CCl_3C_5H_8$	$CHCl_3$	C_2Cl_6
Yield (%)*	4	6	29	2	4

* Yields are mole % relative to the total products.

Photochemical Reaction of Bicyclo[2.1.0]pentane with Bromotrichloromethane.—The products of the photochemical reaction of (1) with bromotrichloromethane, together with their proportions, are given in Table 2. The reaction was stopped at <50% consumption of (1). Photolysis of CCl_3Br produces trichloromethyl radicals and bromine atoms. The presence of *cis*- and *trans*-1,3-dibromocyclopentane indicates that the bromine atoms take part in an S_H2 reaction with (1) in essentially the same way as described above. The final bromine abstraction step of the intermediate 3-bromocyclopentyl radicals now involves CCl_3Br, and the *trans* : *cis* ratio is higher (6.0) as would be expected. *cis*- and *trans*-1-Bromo-3-chlorocyclopentane were also important products in the 4 h photolyses. These could have been formed by 3-bromocyclopentyl radicals abstracting chlorine from CCl_3Br, but a more likely route would seem to be *via* 3-chlorocyclopentyl radicals formed by an S_H2 attack of chlorine atoms on (1) with subsequent bromine abstraction. Chlorine atoms are not formed in significant amounts in the initial photolysis of CCl_3Br [12] and therefore they probably arise by photolysis of products such as C_2Cl_6. The proportion of the chlorobromocyclopentanes was much less in photolyses lasting shorter times which supports this idea.

Bromocyclopentane and chlorocyclopentane are probably formed in part *via* the corresponding 3-halogenocyclopentyl radicals and in part by reaction of (1) with the corresponding hydrogen halide. Even if chlorine atoms react with (1) exclusively by the S_H2 process some HCl will be formed in the later stages of the reaction by abstraction from the products.

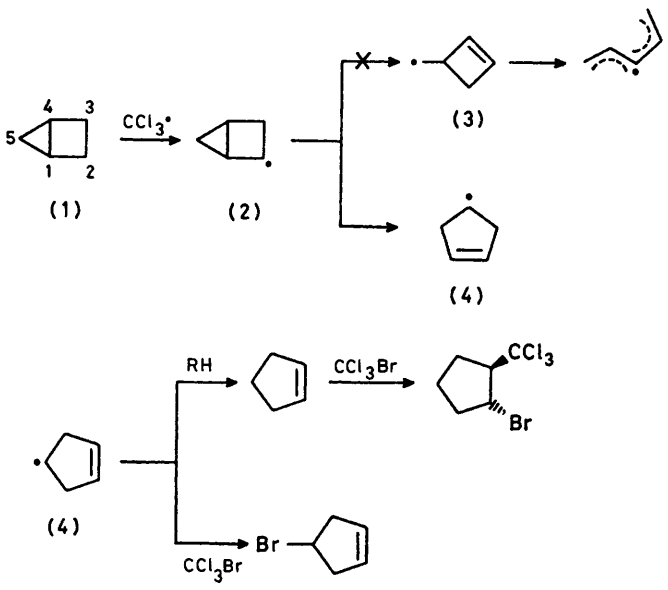
The remaining products: cyclopentene, 4-bromocyclopentene, *trans*-1-bromo-2-(trichloromethyl)cyclopentane, chloroform, and hexachloroethane, arise by hydrogen abstraction from (1) and combination of trichloromethyl radicals. Hydrogen abstraction would be expected to occur at C(2) or C(3) of the cyclobutyl ring since abstraction from cyclopropane is known to be much slower.[13,14] The resulting bicyclopent-2-yl radicals (2), like cyclopropylmethyl radicals, can ring open by fission of a β-C–C bond. The two possible modes of ring opening are shown in Scheme 2.

Fission of the C(1)–C(5) bond would give cyclobutenylmethyl radicals (3) which in turn could ring open to pentadienyl radicals. The observed products show that this does not happen; instead fission of the C(1)–C(4) bond occurs with formation of the cyclopent-3-enyl radical (4) which abstracts hydrogen or bromine from the reactants to give cyclopentene and 4-bromocyclopentene.

The β-scission of cyclopropylcarbinyl radicals normally proceeds most readily when the semi-occupied orbital can assume an eclipsed conformation with respect to the β, γ bond.[15,16] In radical (2) this would appear to favour scission of the C(1)–C(5) bond. Furthermore, *if* the enthalpy barrier to ring opening of cyclobutenylmethyl (3) were small there would be an additional driving force favouring this mode of scission since ring strain could be relieved completely and the resonance energy of pentadienyl could be gained.

Why then does radical (2) undergo scission at its C(1)–C(4) bond? The answer must lie in the fact that this

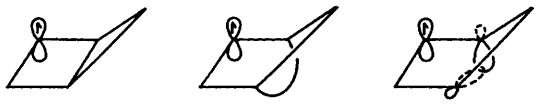
leads to the immediate relief of almost all the ring strain, only the minor cyclopentenyl ring strain remaining in the product radical (4). However, despite the favourable energetics of C(1)–C(4) scission, a high activation energy would be expected for this process unless there was appreciable overlap between the semi-occupied orbital at



SCHEME 2

C(2) and the orbital forming the C(1)–C(4) bond. Such overlap is not apparent in a simple drawing of radical (2), *e.g.* (2a). This bond is probably formed from orbitals having an appreciable percentage of *p* character. As a consequence, the C(1)–C(4) bond is somewhat ' bent ', being intermediate in length between the bonds of cyclobutane and cyclopropane.[2] The bent C(1)–C(4) bond overlaps quite nicely with the semi-occupied orbital, see *e.g.* (2b or c).

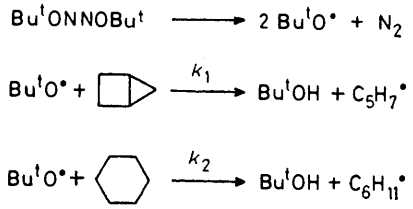
The *trans*-1-bromo-2-(trichloromethyl)cyclopentane is probably formed by radical chain addition of bromotrichloromethane to the product cyclopentene. It was difficult to distinguish this compound from the *trans*-1,3-isomer which would be formed by S_H2 attack of ·CCl_3 radicals on (1). The mass, i.r., and ^1H n.m.r. spectra (which consists of a series of poorly resolved multiplets) appeared to be consistent with either isomer in the



absence of authentic standards. The structure was therefore established by synthesis of the *trans*-1,2-isomer from photochemical addition of CCl_3Br to cyclopentene. The authentic material was spectroscopically and chromatographically identical with the compound isolated from the bicyclopentane reaction mixture. The absence of *trans*- and *cis*-1-bromo-3-(trichloromethyl)cyclopentane from the reaction mixture shows that CCl_3· radicals *exclusively* abstract hydrogen from (1) and do not take part in an S_H2 process.

Reaction of Bicyclo[2.1.0]*pentane with t-Butoxyl Radicals.*—Photolysis of (1) in CCl_3Br solution to which t-butyl hypochlorite was very slowly added gave rise to a complex mixture of products. t-Butyl alcohol, 4-bromocyclopentene, chlorocyclopentane, *trans*-1,2-dichlorocyclopentane, *trans*-1,3-dichlorocyclopentane, and *trans*-1-bromo-3-chlorocyclopentane were identified, but there were at least 16 other minor unidentified components. Walling and Padwa found that under conditions of slow addition of Bu^tOCl to a hydrocarbon in CCl_3Br, the main chain carrying radical is t-butoxyl.[17] The presence of Bu^tOH and 4-bromocyclopentene, which was the main product in the initial stages of the reaction, suggests that Bu^tO· radicals abstract hydrogen from C(2) or C(3) in (1) with subsequent ring opening of the radical (2) and bromine abstraction from the solvent as in Scheme 2. Chlorine atoms, also generated in the photodecomposition of Bu^tOCl, take part in an S_H2 reaction at C(1) or C(4) of (1) to give 3-chlorocyclopentyl radicals. These radicals can abstract chlorine from Bu^tOCl or bromine from the solvent. The retention times and mass spectral evidence suggest that the unidentified components are mostly polyhalogenated compounds.

Chlorocyclopentane is probably formed in this system (as in the neat CCl_3Br system) both by reaction of (1) with HCl and by hydrogen abstraction from (1) by 3-chlorocyclopentyl radicals. It seemed likely that the



SCHEME 3

latter reaction should be relatively unimportant because alkyl radicals are known to abstract hydrogen from alkanes much more slowly than they abstract halogen from CCl_3Br or t-butyl hypochlorite.[18] However, there was the possibility that (1) was a much better hydrogen atom donor than most alkanes because the abstraction of hydrogen might be assisted by energy released in a *concerted* opening of the C(1)–C(4) bond. If this were the case it would, of course, imply that radical (2) was not a discrete intermediate that could be formed by hydrogen abstraction from (1).

To check whether or not (1) is an exceptionally good hydrogen donor its reactivity towards t-butoxyl radicals relative to cyclohexane was measured by a competitive procedure (Scheme 3). The t-butoxyl radicals were generated by the thermal decomposition of t-butyl hyponitrite for 20 half-lives at 50 °C in benzene as solvent. From the amounts of (1) and C_6H_{12} consumed the molar rate constant ratio, k_1/k_2 is calculated [19] to be *ca.* 0.62.

This means that (1) is not an unusually good hydrogen donor and so the halogenocyclopentanes are probably not formed to any large extent by abstraction from (1) by 3-halogenocyclopentyl radicals. On the other hand, (1) has only four reactive hydrogens [or possibly only two if the cyclopropyl ring hinders attack on the *cis* C(2) and C(3) hydrogens] whereas cyclohexane has twelve reactive hydrogens. This means that the reactive C–H bonds in (1) are more readily broken than those in cyclohexane–which makes them considerably more reactive than the C–H bonds in cyclobutane, rather than less reactive as is normally observed.[20] There is therefore a distinct possibility that (2) is not an intermediate in hydrogen atom abstraction from (1).

In an attempt to observe (2) by e.s.r. spectroscopy, (1) and di-t-butyl peroxide (neat, or in cyclopropane, or ethylene) were photolysed directly in the cavity of a Varian E-4 e.s.r. spectrometer. A spectrum having g 2.002 98 which could be analysed in terms of hyperfine splitting by one α-hydrogen (a_α 21.2 G), four equivalent β-hydrogens (a_β 36.9 G), and two equivalent γ-hydrogens (a_γ 0.46 G), together with some partly resolved second-order lines, was observed at temperatures from −160 °C (in ethylene) to +100 °C (neat). This spectrum could not come from radical (2) but the e.s.r. parameters are entirely consistent with those expected for the cyclopent-3-enyl radical (4). This result lends further support to the idea that t-butoxyl radicals react with (1) mainly, if not exclusively, by abstracting hydrogen from the C(2) position. Finally, the absence of a spectrum attributable to radical (2) implies, under our conditions, that the rate constant for its rearrangement to radical (4) is $\geqslant 10^2$ s^{-1} at −160 °C. If we assume a 'normal' A factor of 10^{13} s^{-1} for this reaction, then the activation energy for the ring opening must be $\leqslant$24 kJ mol^{-1}.

Photochemical Reaction of Bicyclo[2.1.0]*pentane with* N-*Bromosuccinimide*.—When bicyclopentane and *N*-bromo succinimide (NBS) are stirred at ambient temperature in the presence of light from a tungsten bulb a slow reaction takes place to give five main products, succinimide, 4-bromocyclopentene, *cis*- and *trans*-1,3-dibromocyclopentane, and minor amounts of *trans*-1,2-dibromocyclopentane. The proportions of the bromo-compounds are given in Table 3.

The 1,3-dibromides clearly result from bromine atoms attacking (1) at C(1) or C(4) in the usual S_H2 process. The 3-bromocyclopentyl radicals evidently abstract bromine from NBS and not from molecular bromine, since the *trans* : *cis* ratio (*ca.* 3.5 : 1) is appreciably higher than that found with molecular bromine.[11] The major process in the early stages of the reaction (see Table 3) is hydrogen abstraction from (1) giving eventually 4-bromocyclopentene, the only uncertainty being the attacking radical. At first sight it might appear that 'allylic' bromination is occurring here adjacent to the 'pseudo- π-system' of the cyclopropane ring. The accepted Goldfinger mechanism for allylic bromination of alkenes by NBS relies on a *reversible* addition step to the π-bond of the alkene. At the low bromine concentration supplied by NBS the equilibrium in the addition step lies to the left and allylic abstraction is favoured over addition.[21] In the bromination of (1), however, the step analogous to addition is actually a radical displacement reaction (S_H2) at the cyclopropyl ring. It is quite unreasonable to propose that this step could be reversible, and therefore an 'allylic' type of bromination cannot occur. The radical responsible for hydrogen abstraction cannot be bromine but is most likely succinimidyl.

TABLE 3

Products and yields (%)* of reaction of bicyclopentane with *N*-bromosuccinimide at ambient temperature

t/h	4-Bromocyclopentene	*trans*-1,2-Dibromocyclopentane	*trans*-1,3-Dibromocyclopentane	*cis*-1,3-Dibromocyclopentane
37	52		37	10
44	52	2	36	10
61	42	2	42	12
64	36	3	47	14
92	23	4	50	23

* Yields as mole % relative to the total products.

Bromination of alkylcyclopropanes in the side chain by NBS has also been interpreted in terms of hydrogen abstraction by succinimidyl radicals.[22,23]

Conclusions.—Bicyclo[2.1.0]pentane can take part in two basic types of radical reaction. Firstly, halogen atoms react mainly, but not exclusively, by S_H2 attack at the bridgehead atoms C(1) or C(4) to give 3-halogenocyclopentyl radicals. Secondly, trichloromethyl, t-butoxyl, and probably succinimidyl radicals abstract the most weakly bound hydrogens at C(2) and C(3) in the cyclobutane ring. This would yield bicyclopent-2-yl radicals (2) but these could not be observed by e.s.r. spectroscopy nor trapped even with such good carbon radical scavengers as Br_2, CCl_3Br, and Bu^tOCl. It is possible that (2) does not exist as a discrete intermediate, in which case hydrogen abstraction from the cyclobutane ring yields cyclopent-3-enyl radicals directly.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian EM 360 and/or HA-100 instruments in CCl_4 solutions at room temperature with tetramethylsilane as internal standard. The ^{13}C n.m.r. spectra were recorded on a Varian CFT 20 spectrometer. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. G.l.c. analyses were carried out on a Pye 105 instrument with columns packed with Embaphase silicone oil, tritolyl phosphate, and ββ′-oxydipropionitrile on Chromosorb G as solid support.

Bicyclo[2.1.0]pentane (1) was prepared from cyclopentadiene and diethyl azodicarboxylate, *via* diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate and 2,3-diazabicyclo[2.2.1]hept-2-ene by the method of Gassman and Mansfield.[24] The spectral and other characteristics of the product agreed with those in the literature, and it was shown by g.l.c. to be >98% pure.

Bromination of (1) *with Molecular Bromine*.—Bromine (25 μl) in CCl_4 (500 μl) was added dropwise to a solution of (1) (100 μl) in CCl_4 (500 μl) maintained at 0 °C. A vigorous reaction occurred in daylight and the bromine colour disappeared immediately. G.l.c. analysis of the mixture

showed four main components. A reaction with excess bromine was carried out in a similar way, and showed the same four components. Coupled g.l.c.–mass spectrometry showed the first component to be bromocyclopentane and the last three components to be isomeric dibromocyclopentanes. They were then tentatively identified by comparison of their retention times with authentic dibromocyclopentanes prepared by bromination of bromocyclopentane.[25] Finally, (1) was brominated on a larger scale and the components separated by preparative g.l.c. on a 15 ft silicone oil column at 150 °C. The ^1H and ^{13}C n.m.r. spectra of the first eluted product confirmed it as bromocyclopentane: peak 2, δ_H 2.0—2.4 (4 H), 2.5—2.9 (2 H), and 5.3 (2 H), δ_C 56.44, 33.68, and 20.94 p.p.m.; peak 3, δ_H 2.0—2.4 (2 H), 2.4—2.8 (4 H), and 4.4—4.6 (2 H), δ_C 49.59, 47.61, and 35.99 p.p.m.; peak 4 δ_H 2.2—3.1 (6 H) and 4.0—4.3 (2 H), δ_C 48.18, 44.10, and 36.52 p.p.m. Comparison of these ^1H n.m.r. spectra with those of dichlorocyclo-pentanes [26,27] and bromochlorocyclopentanes [28] established their identity as *trans*-1,2-dibromocyclopentane, *trans*-1,3-dibromocyclopentane, and *cis*-1,3-dibromocyclopentane, respectively.

The chromatograms also showed the presence of two trace products. These were tentatively identified as cyclopentene and 4-bromocyclopentene by retention time comparisons with authentic samples.

Bromination was attempted using neat bromine and neat (1). The reaction was extremely vigorous and the chromatograms of the resulting mixture showed a very large number of components which were not analysed further.

Photochemical Reaction of Bromotrichloromethane with (1).—Bromotrichloromethane (0.6 g) and (1) (0.21 g) were photolysed at ambient temperature in a Pyrex tube with light from a Hanovia UVS 220 medium pressure mercury arc. The solution was sampled from time to time and analysed by g.l.c. on a 15 ft column of 10% silicone oil at 145 °C. Products were identified by coupled g.l.c.–mass spectrometry which indicated the following: peak 1, cyclopentene; peak 2, chloroform; peak 3, chlorocyclopentane; peak 4, 4-bromocyclopentene; peak 5, bromocyclopentane; peak 6, *trans*-1-bromo-2-chlorocyclopentane; peak 7, *trans*-1-bromo-3-chlorocyclopentane; peak 8, *cis*-1-bromo-3-chlorocyclopertane; peak 9, hexachloroethane; peak 10, *trans*-1,3-dibromocyclopentane; peak 11, *cis*-1,3-dibromocyclopentane; peak 12, an isomer of the bromo(trichloromethyl)cyclopentane family. The identities of peaks 1, 2, 3, 5, and 9 were confirmed by retention time comparisons with commercial samples. The dibromocyclopentanes were confirmed by retention time comparisons with authentic samples prepared as described above. The chlorobromocyclopentanes were confirmed by retention time comparisons with authentic samples prepared by chlorination of bromocyclopentane.[25] The identity of peak 4 was confirmed by comparison with authentic material.[28] Material corresponding to peak 12 was separated by preparative g.l.c. and its retention time, i.r., ^1H n.m.r., and mass spectra shown to be identical with those of authentic *trans*-1-bromo-2-(trichloromethyl)cyclopentane (see below). The proportions of the various products after 4 h photolysis are shown in Table 2. No products were visible on the chromatogram until >15 min photolysis. In the early stages of the reaction (1—2 h) 4-bromocyclopentene and *trans*- and *cis*-1,3-dibromocyclopentane formed a much greater percentage of the total products.

trans-1-*Bromo*-2-(*trichloromethyl*)*cyclopentane*.—Cyclopentene (0.2 g) and CCl_3Br (1 g) were photolysed at ambient temperature in a Pyrex tube by light from a Hanovia UVS 220 mercury arc. After 1 h the mixture was analysed by g.l.c. and the product isolated from unchanged reactants by preparative g.l.c. on a 7 ft column of 10% silicone oil at 150 °C. $C_6H_8{}^{35}Cl_3{}^{79}Br$ had M^+ 264 followed by a series of isotopic clusters corresponding to successive loss of halogens, $\nu_{max.}$ (liquid film) 2 950, 2 850, 1 430, 1 190, 1 050, 1 005, 900, 855, 790, and 760 cm^{-1}, δ_H 1.7—2.4 (6 H), 3.6 (1 H), and 4.5 (1 H).

Photochemical Reaction of (1) *with* Bu^tOCl *in* CCl_3Br *Solution*.—To (1) (0.2 g) in CCl_3Br (1 g) was added Bu^tOCl (0.2 g) in a very slow stream from a narrow dropper. The mixture was photolysed at ambient temperature in a Pyrex tube by light from a UVS 220 mercury arc. The mixture was analysed every few minutes and the reaction stopped after 15 min when photodecomposition of the CCl_3Br becomes significant (see above). The product chromatogram showed the presence of t-butyl alcohol, chlorocyclopentane, 4-bromocyclopentene, bromocyclopentane, *trans*-1,2-dichlorocyclopentane, *trans*-1,3-dichlorocyclopentane, *trans*-1-bromo-3-chlorocyclopentane, and at least 16 other minor components. The identities were established by coupled g.l.c.–mass spectrometry and by retention time comparisons with authentic materials. The mass spectra suggested that most of the unidentified components were polyhalogenated compounds. Quantitative analysis was not attempted, but 4-bromocyclopentene was the main product in the early stages of photolysis.

Thermal Reaction of (1) *with* $Bu^tONNOBu^t$.—A solution of (1) (0.250 mol dm^{-3}), cyclohexane (0.206 mol dm^{-3}), and t-butyl hyponitrite (0.108 mol dm^{-3}) in benzene was degassed, sealed under vacuum, and then heated at 50 °C for 37 h (*ca.* 20 half-lives of the $Bu^tONNOBu^t$). n-Octane (0.139 mol dm^{-3}) was added to the opened tube as an internal standard and the reactants and products were analysed by g.l.c. on a 24 ft 20% Carbowax 20 M column at 60 °C. The concentrations of unchanged (1) and cyclohexane were 0.204 and 0.148 mol dm^{-3}, respectively. Although only 0.104 mol dm^{-3} of the starting hydrocarbons were consumed by *ca.* 0.2 mol dm^{-3} of t-butoxyl radicals (confirmed by the yield of Bu^tOH) this ' wastage ' was expected since the olefinic products which must be formed in this reaction will be much more reactive towards $Bu^tO\cdot$ than the starting materials. Furthermore, some cyclohexane [and possibly some (1)] will be reformed in radical–radical disproportionation reactions; which adds some uncertainty to the calculated $k_1 : k_2$ ratio.

Photochemical Reaction of (1) *with* NBS *in* CCl_4 *Solution*.—Compound (1) (0.5 g) and NBS (1.3 g) in CCl_4 (5 g) were stirred at ambient temperature under illumination from a tungsten lamp. The mixture was analysed periodically by g.l.c. The reaction was stopped after 92 h when the mixture turned brown. Succinimide, m.p. 126 °C, was filtered off. The solution contained 4-bromocyclopentene, *trans*-1,2-dibromocyclopentane, *trans*-1,3-dibromocyclopentane, and *cis*-1,3-dibromocyclopentane whose identities were confirmed in the same way as described above.

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