cationic intermediate **8b** is then trapped by bromide ion attacking from the back side equatorially. When cation **8** (X = Br) rearranges to the corresponding intermediate **9**, the attack of bromide ion gives **5**. Alternatively, when bromine initially attackds double bond B in **1**, the cationic intermediate **6** (X = Br) is formed and rearranges to **7**, and these cations are trapped by bromide ions to give **4** and **5**. It is interesting that the bromination of **1** gives dibromides with skeletal rearrangement in contrast to oxymercuration of **1**, which gives **2** and **3a** without skeletal rearrangement. We suggest that after the attack of bromine, a counter bromide ion remains as a stable ion until the equilibria **6** ⇌ **7** and **8** ⇌ **9** (X = Br) are established. The more reactive acetate anion, however, can trap the cationic intermediates **6** and **8** (X = Hg) before the corresponding equilibria are established.

Experimental Section[7]

Bromination of 1. (8*SR*,12*RS*)-3,4-Benzo-8,12-dibromotetracyclo[5.4.0.$1^{2,6}$.$0^{5,9}$]dodec-3-ene (**3b**), (5*RS*,9*SR*)-2,3-benzo-5,9-dibromotetracyclo[4.3.3.$0^{4,8}$.$0^{7,10}$]dodec-2-ene (**4**), and (9*SR*,12*RS*)-2,3-benzo-9,12-dibromotetracyclo[4.3.3.$0^{4,10}$.$0^{8,11}$]dodec-2-ene (**5**). To a solution of **1** (165 mg, 0.75 mmol) in CCl_4 (5 mL) was added a solution of bromine (125 mg, 0.78 mmol) in CCl_4 (3 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C. After workup, the CCl_4 layer was dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel eluting with hexane–chloroform (10:1). From the first fraction, a mixture of **3b** and **5** (133 mg) was collected. The mixture was taken up in ethanol (1 mL) and, after 30 min in a refrigerator, **5** crystallized out as colorless crystals. After the filtrate was concentrated, the residue was taken up hexane (1 mL) and allowed to stand for 24 h in a refrigerator, and **5** and **3b** were crystallized out as colorless block crystals and fine needles, respectively. The crystals of **3b** and **5** were separated with a spatula. The ratio of **3b** to **5** was determined from the ^{1}H NMR spectra of the mixture as 6:17. From the second fraction, 78 mg (27.6%) of **4** was obtained. From a third fraction, 64.4 mg of uncharacterized oil was collected.

3b (11.9%); mp (EtOH) 105–106 °C; ^{1}H NMR δ 0.40 (1 H, m), 0.96 (1 H, dd, J = 10 Hz), 1.62 (1 H, m), 1.96 (1 H, m), 2.66 (2 H, d, J = 8 Hz), 3.18 (1 H, q), 3.37 (1 H, m), 3.25 (1 H, dd, J = 8 Hz, J = 3 Hz), 3.64 (1 H, t, J = 9 Hz), 3.90 (1 H, s), 4.49 (1 H, m), 6.80–7.28 (4 H, m); IR (Nujol) 798, 759, 740, 725 cm^{21}; UV λ_{max} (EtOH) 274 (ε, 596), 267 (697), 261 (540), 204 nm (25 100). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 52.11; H, 4.38.

4 (27.6%); mp (EtOH) 162–162.5 °C; ^{1}H NMR δ 0.1 (1 H, m), 1.5–1.75 (3 H, m), 2.88 (1 H, q), 3.0–3.4 (3 H, m), 3.56 (1 H, q, J = 15.8 Hz), 3.86 (1 H, d, J = 7 Hz), 4.40 (1 H, s), 4.56 (1 H, t, J = 4 Hz), 6.97 (1 H, d), 7.1–7.3 (3 H, m); IR (Nujol) 1590, 816, 789, 772 cm^{-1}; UV λ_{max} (EtOH) 277 (ε, 379), 269 (454), 226 (7330), 204 nm (37 700). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 51.98; H, 4.31.

5 (34.2%): mp (EtOH) 119.5–120.5 °C; ^{1}H NmR δ 1.30 (1 H, m), 1.08 (1 H, dd, J = 14 Hz, J = 13 Hz), 1.7 (1 H, m), 1.98 (1 H, m), 2.60 (1 H, m), 2.94 (1 H, m), 3.4–3.6 (2 H, m), 4.34 (1 H, s), 4.54 (1 H, t, J = 5 Hz), 7.1–7.4 (4 H, m); IR (Nujol) 1575, 764, 745 cm^{-1}; UV λ_{max} (EtOH) 277 (ε, 290), 270 (400), 264 (939), 204 nm (35 000). Anal. Calcd for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 52i.21; H, 4.18.

Acknowledgment. The author is especially appreciative of synthetic work performed by S. Sagara, ^{1}H NMR measurements by K. Sasaki, Tohoku University, and Professor K. Hosokawa, Kawasaki Medical College, for encouragement. This investigation was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education in Japan, Science and Culture (No. 58540136).

Registry No. **1**, 82730-02-7; (±)-**3b**, 95647-64-6; (±)-**4**, 95647-65-7; (±)-**5**, 95647-66-8; Br_2, 7726-95-6.

Supplementary Material Available: ^{1}H NMR spectra of **3b**, **4**, and **5** (29 pages). Ordering information is given on any current masthead page.

(7) All melting points are uncorrected. Infrared spectra were obtained on a JASCO IRA-1 spectrometer. Ultraviolet spectra were measured with a Hitachi UV-200 spectrometer. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer (200 MHz) in $CDCl_3$ with tetramethylsilane as an internal standard.

The Mixed-Chain Alternative to the Postulated π and σ Reactivities of the Succinimidyl Radical: Cyclopentane/Cyclohexane. A Critical Examination of the Rebuttal of the Previous Report

D. D. Tanner,* C. P. Meintzer, and S. L. Tan

Department of Chemistry, The University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Received July 17, 1984

Recently we have reported that the mechanism of the competitive photobromination reactions of cyclopentane and cyclohexane with *N*-bromosuccinimide (NBS) proceeded by a bromine atom chain in solvents where NBS was insoluble or initially by a succinimidyl radical chain in solvents, acetonitrile, or methylene chloride, where the NBS is soluble.[1] As these latter reactions progressed, the bromine atom chain begins to dominate the reaction. Limiting conditions were developed for the reaction where either ethylene was added to limit the bromine atom chain or molecular bromine was added to limit the incursion of succinimidyl radical chemistry. In all of the reactions run with NBS, NBS–Br_2, or NBS–olefin substantial amounts of ring-opened material β-bromopropionyl isocyanate (β-BPIC) were formed. The relative reactivity of cyclopentane/cyclohexane, k_5/k_6, was established as 9.2 for bromine atom abstraction, without reversal, and 0.82 for the succinimidyl radical reactivity.[2]

Subsequent to this publication a report appeared which attempted to explain the observations reported as being due to a mixture of three chains carried by the π- and σ-succinimidyl radicals and by the bromine atom as well.[3] Limiting conditions were reported which supposedly identified the reactivity of the three abstracting species. The contents of the paper consisted of five single experiments.

Two of these reactions, the reactions of the cycloalkanes with NBS–olefin (1,1-dichloroethene) (method "Sσ" of ref 3) and the reaction with molecular bromine (method D of ref 3), showed relative reactivities, 0.88 (0.81)[4] and 8.8, which were in close agreement with the values reported in our original publication[1] and which had been attributed to the reactivity of the succinimidyl radical (NS·) and the bromine atom (Br·). As was reported previously a major

(1) Tanner, D. D.; Ruo, T. C. S.; Takiguchi, H.; Guillaume, A.; Reed, D. W.; Setiloane, B. P.; Tan, S. L.; Meintzer, C. P. *J. Org. Chem.* **1983**, *48* 2743.

(2) The value k_5/k_6 was found to be somewhat solvent and concentration dependent. The value 9.2 for bromine atom abstraction was established from reaction run to low conversion in liquid bromine[1] while the value of 0.82 was obtained from reactions run in CH_2Cl_2 as solvent and CH_2=CH_2 as the bromine atom trap. Some small variation in the efficiency of trapping bromine by CH_2CCl_2 or CH_2=CH_2 may lead to small variations in the relative rate values obtained for succinimidyl radical abstraction.

(3) Skell, P. S.; Seshadri, S. *J. Org. Chem.* **1984**, *49*, 1650.

(4) In ref 3 the [c-C_6H_{12}] for methods: Sσ, Sπ method A, and Sπ method B should have read 1.41 M rather than 1.54 M. The new concentration changes the reported relative rates, k_5/k_6, to 0.81, 1.1, and 1.2.

0022-3263/85/1950-1534$01.50/0

Table I.[a] The Photobromination of Cyclopentane/Cyclohexane with NBS–Br_2 (15 °C)

additive (M)	reactn,[c] %	yield of products,[c] %						
		c-C_5H_9Br	c-$C_6H_{11}Br$	c-$C_5H_8Br_2$	c-$C_6H_{10}Br_2$	β-BPIC	NSH	k_5/k_6[f]
Br_2 (0.028)[b]	100+[d]	57.2	5.59	NR	NR	0	100	9.0 (1)
Br_2 (0.029)	89.5	37.6 ± 0.8	6.10 ± 0.07	13.7 ± 0.4	0.16 ● 0.03	9.90 ± 0.79	72.7 ± 3.4	7.1 ± 0.1 (3)
Br_2 (0.030)	71.5	49.2	7.2	11.6	tr	8.0	69.9	7.3
Br_2 (0.030)	73.7	45.2	7.3	14.4	tr	8.3	75.7	7.1
Br_2 (0.020)	68.8	54.2	7.6	10.0	0.11	6.3	76.7	7.2
Br_2 (0.010)[e]	60.2	72.5	9.4	4.5		13.4	87.2	8.3

[a] Unless otherwise listed the basic recipe consisted of the following: [c-C_5H_{10}], 1.00 mL (10.6 mmol); [c-C_6H_{12}], 1.00 mL (9.25 mmol); NBS, 0.30 g (1.7 mmol); CH_2Cl_2, 5.0 mL, and the added bromine. [b] Taken from ref 2, Skell and Seshadri. [c] Percentage based on [NBS]^{used}. [d] The reaction was carried out until all of the NBS, and added bromine had been consumed. [e] Taken from ref 1, a homogeneous mixture of the following: c-C_5H_{10} (0.427 M), c-C_6H_{12} (0.434 M), NBS (0.0359 M), and Br_2 (9.78×10^{-3} M) in CH_2Cl_2. [f] Numbers in parentheses are numbers of independent experiments reported.

product formed in the reaction carried out with the NBS–olefin reagent was the ring-opened material β-BPIC.

The third of the five reactions was the bromination of the pair of cycloalkanes with the NBS–Br_2 reagent (method C of ref 3). The authors, using a heterogeneous mixture of NBS (1.7 mmol) and Br_2 (0.2 mmol) in 7 mL of a solution of the two substrates (cyclopentane and cyclohexane) in methylene chloride (1:1:5), photolyzed the mixture until all of the active halogen had been consume.[5] They obtained a relative reactivity, $k_5/k_6 = 9.0$, attributable to the bromine atom, but unlike our original publication[1] they detected no β-BPIC. The original experiments[1] were run from 40 to 96% reaction at near the saturation concentration (0.068 M) for that mixture. The reaction has now been carried out under the new conditions proposed[3] to be those which can be used to show the reactivity of the π-succinimidyl radical with unreactive substrates or to give bromine atom reactivity for more reactive substrates. In either case no β-BPIC should be formed. Contrary to the latest report,[3] when the reaction was carried out so that the solubility of NBS was always exceeded (<74% reaction under the conditions prescribed) an intermediate value ($k_5/k_6 = 7.1 \pm 0.1$) for the relative reactivity of the two substrates was obtained (i.e., intermediate between the bromine atom and succinimidyl radical reactivity) and an appreciable amount of β-BPIC, 7.2 ± 0.7%, was formed; see Table I. The relative reactivities and yield of β-BPIC reported in the original manuscript[1] were in excellent agreement with results obtained by using the newly suggested recipe. A comparison of the original results carried out under homogeneous conditions,[1] the results obtained by Skell and co-workers with nonhomogeneous mixtures,[3] and a reexamination of the new method are listed in Table I. Since the pure succinimidyl chain, $k_5/k_6 = 0.82$, had been reported to yield [β-BPIC] ≃ 40% of the NBS reacted,[1] a 7–10% yield was consistent with a mixed chain having an intermediate value of k_5/k_6. We believe that the difference between our results and those reported by Skell[3] lies in the analytical techniques employed. It is clear from the 200-MHz ^1H NMR spectra that the nominal pair of triplets attributable to ring-opened material is assignable to the absorbance of the methylene protons of β-bromopropionamide (β-BPA). In this solvent system the (Figure 1) absorbance of the methylene protons of β-BPIC have chemical shifts centered at δ 3.6 and 3.1. Reaction mixtures which contained low

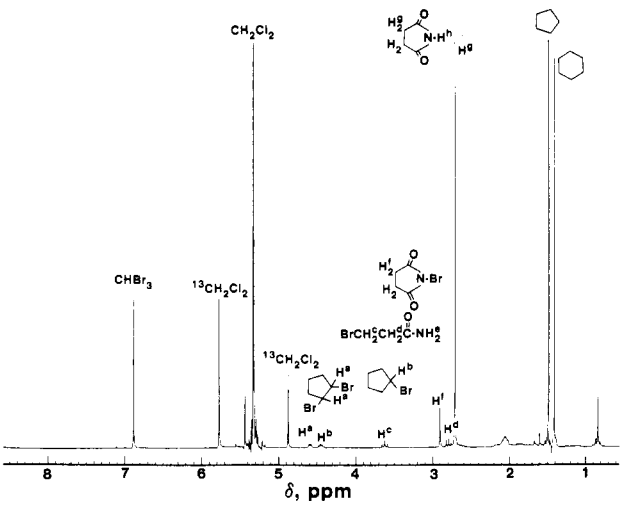


Figure 1. The 200-MHz ^1H NMR spectrum of the reaction mixture from the photobromination of cyclopentane and cyclohexane with NBS–Br_2 in dichloromethane (48 scans). (N–H^h is at δ 8.24; C(=O)NH_2^e is at δ 6.2).

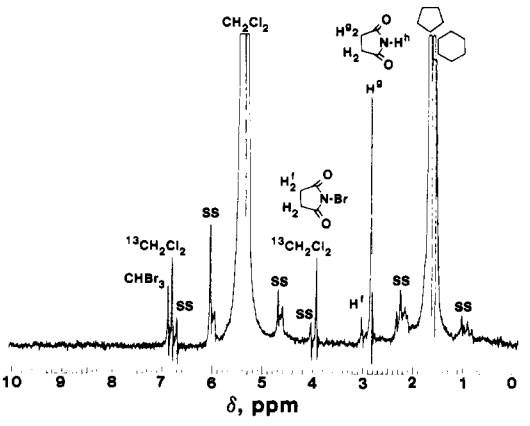


Figure 2. The 60-MHz ^1H NMR spectrum (Varian EM-360) of the reaction mixture from the photobromination of cyclopentane and cyclohexane with NBS–Br_2 in dichloromethane (SS = "spinning sideband"; NH^h too broad).

percentages of β-BPIC showed that the β-BPIC underwent almost quantitative hydrolysis by the residual water contained in commercial or repurified NBS, and as is the case with other substrates which give higher yields of β-BPIC, mixtures of the isocyanate and its hydrolysis product are always detected.[6] In the experimental technique described by Skell and co-workers,[1,7] and used by them in their study

(5) Originally[6b,c] the conditions prescribed to observe π-NS· chemistry using the NBS/Br_2 reagent was given as [Br_2] > 10^{-3} M, [NBS] = 0.22 M; no limit was placed upon the percentage conversion (14–96%).

Although the authors had criticized the original publication[1] for using concentrations of NBS and bromine which were too low (NBS, 0.04 M; Br_2, 0.002–0.01 M) and for allowing their concentrations to diminish during the course of the reaction[3] they chose to run the reactions to completion and to allow the added molecular bromine to completely react.

(6) The presence of residual water in purified NBS has been noted previously. See: Dauben, H. J.; McCoy, L. L. *J. Am. Chem. Soc.* **1959**, *81*, 4863. A minimum amount of water was determined for the purified NBS used. (See Experimental Section).

Table II.[a] Photoinitiated NBS Bromination of c-C_5H_{10} and c-C_6H_{12} in CH_2Cl_2 with added CH_2CCl_2 and $BrCCl_3$ or CCl_4 (15 °C)

additive (mL)	reactn,[b] %	yield of products,[b] %								
		c-C_5H_9Br	c-$C_6H_{11}Br$	c-$C_5H_8Br_2$	c-$C_6H_{10}Br_2$	$CHCl_3$	Cl_3C–CCl_3	$BrCH_2CCl_2Br$	β-BPIC	k_5/k_6
$BrCCl_3$ (2.0)[c]	NR	1.4	0.94	NR	NR	0	NR	NR	0	(1.1)[c]
$BrCCl_3$ (2.0)	9.1–12.0[d]	1.2 ± 0.2	1.2 ± 0.2	0	0.032 ± 0.021	0	0	0.51 ± 0.22	0	0.80 ± 0.06
$BrCCl_3$ (2.0)	18.0	26.4	31.1	0.18	2.41	0.72	0.28	6.40	2.02	0.62
CCl_4 (2.0)	8.7	1.7	1.9	0	0			0	0	0.70
CCl_4 (2.0)	15.7	2.8	3.1	0	0			0.032	0	0.71
CCl_4 (2.0)	27.9	8.4	9.3	0	0.13			0.10	2.9	0.70
CCl_4 (1.25)[e]	8.7	1.6	1.6	0	0			0	0	0.79
CCl_4 (1.25)	10.7	2.9	3.2	0	0			0	0	0.71
CCl_4 (1.25)	26.2	7.7	8.5	0	0			0	2.3	0.71

[a] The cycloalkanes, 1.00 mL (10.6 mmol) of cyclopentane and 0.90 mL (8.33 mmol) of cyclohexane, NBS (0.30 g, 1.7 mmol), and CH_2CCl_2 (0.080 mL, 1.01 mmol) in 2.0 mL of CH_2Cl_2 was used as the basic mixture. [b] Percentage based on NBS[0]; NR, not reported. [c] Taken from ref 2, Skell and Seshadri, see ref 3. [d] Three independent experiments. [e] Saturation solubility of NBS with added $BrCCl_3$ and CCl_4 (1.25 mL) are equal at 0.02 M.

on cyclopentane and cyclohexane, β-BPIC was detected qualitatively by the presence or absence of its strong IR absorption peak at 2245 cm^{-1} and only if detected was it quantitatively determined by 60-MHz proton NMR after its distillation, in vacuo, from the reaction mixture. This method of analysis ensured that moderate amounts of β-BPIC could not be detected since hydrolysis would destroy the isocyanate, and the hydrolysis product would not be volatile. When the reaction mixture was analyzed by using the same instrumentation reported by Skell and co-workers (see Figure 2), the β-BPA was only barely distinguishable.

The fourth experiment (method A of ref 3), which presumably showed π-NS· chemistry, was run according to a recipe that called for a heterogeneous mixture of NBS, the two substrates (cyclopentane and cyclohexane), methylene chloride, and vinylidene chloride as well as added bromotrichloromethane. The addition of bromotrichloromethane to the reaction mixture was proposed to function as a source of a stable trichloromethyl radical,[3] which in the absence of molecular bromine (due to the presence of added olefin) acted as a transfer agent to give π-NS· (eq 1–3).

$$CCl_3\cdot + NBS \rightarrow BrCCl_3 + \pi\text{-}NS\cdot \quad (1)$$

$$\pi\text{-}NS\cdot + RH \rightarrow NSH + R\cdot \quad (2)$$

$$R\cdot + BrCCl_3 \rightarrow RBr + CCl_3\cdot \quad (3)$$

Unfortunately, the experiment was run to such low conversion (under 1% of the alkyl bromides formed) that comparable amounts of β-BPIC could not have been detected. We have accordingly reinvestigated the systems together with comparable experiments replacing CCl_3Br with CCl_4, which should not yield $\cdot CCl_3$ but which produces a similar decrease in NBS solubility (see Table II). Skell and co-workers have previously reported[7c] that decreased yields of β-BPIC are obtained as the solubility concentration of NBS is decreased by the addition of another solvent. Even with our more sensitive method of detection it is doubtful that complex mixtures of products, at this level of concentration, could be analyzed by ^1H NMR for ring-opened materials. The relative reactivity, determined by GLPC analysis, however, was intermediate to the limiting values obtained for the succinimidyl and bromine atom chains, and suggested that a mixed chain was involved in the reation. It is clear that the added substrate dramatically decreased the solubility of NBS, and since no chloroform or other products of the reaction of bromotrichloromethane are detected in these low conversion reactions, it was possible that the function of the bromotrichloromethane was only to decrease the concentration of NBS in solution. To check this assumption the reaction was carried out again under exactly the same conditions except that an inert solvent, carbon tetrachloride, was substituted for bromotrichloromethane. The solubility concentration of NBS in this mixture was approximately the same (~0.013 M) as that determined for the mixture containing bromotrichloromethane. An additional experiment using less carbon tetrachloride (1.25 mL), which gave a solution which had the same saturation solubility (0.02 M) as the experiment with added bromotrichloromethane, was also carried out. The results of these three experiments and the one reported by Skell[3] are listed in Table II. At low conversion the relative reactivity of cyclopentane/cyclohexane appeared to indicate the reactivity of a succinimidyl radical chain and at these low concentrations, in agreement with the report of Skell and Seshadri[3] no β-PBIC could be detected. At higher percentage conversion where reliable analysis could be obtained it became obvious that bromotrichloromethane was involved in the reaction, since products of the trichloromethyl radical, chloroform, and hexachloroethane were detected in substantial amounts. Accompanying the formation of the trichloromethyl radical must be the bromine atom (or Br_2), presumably produced by direct photolysis of bromotrichloromethane, but in the presence of olefin the bromine produced did not prevent the production of β-BPIC. At moderately low percentage reaction (18%) the relative reactivity still reflected the reactivity of the succinimidyl radical. The reactions with added carbon tetrachloride were almost identical with those with added bromotrichloromethane except that the reaction was not contaminated by the involvement of the trichloromethyl radical. The mixture showed succinimidyl radical reactivity and no ring-opened product at very low conversion; however, at higher percentage reaction β-BPIC could be detected. It would appear that the relative reactivity and the amount of β-BPIC obtained by adding bromotrichloromethane to the reaction mixture is not indicative of a unique succinimidyl radical but is an artifact of the mixed chain.

The fifth experiment (method B of ref 3), carried out with added benzene, showed the relative reactivity, if one assumes the competitive reactions of a bromine atom and a succinimidyl radical chain, of a slightly contaminated succinimidyl chain, k_5/k_6 = 1.2.[4] At the reported per-

(7) (a) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381. (b) Skell, P. S.; Day, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 1951. (c) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257. (d) Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267. (e) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125.

centage conversion, ~2%, it would not have been possible to detect β-BPIC. When the reaction was carried out to approximately 16% conversion of the initial NBS, the results obtained by Skell[3] could be reproduced. Only 2% of the brominated material was found, and no β-BPIC could be detected, even using the 200-MHz ^1H NMR spectrometer. Like the reactions carried out with added bromotrichloromethane the saturation solubility of NBS was significantly reduced in this mixture (~0.031 M), and the experimental design again must suffer from the same flaw as the previously discussed reaction. In addition to the complication of studying the reaction in nonhomogeneous media the addition of benzene provides a further complication, since benzene itself is a relatively efficient scavenger for the succinimidyl radical.[8-10] The effect of removing succinimidyl radicals is to inhibit both its ability to abstract and its unimolecular formation of ring-opened product. The bromine atoms produced in the reaction are competitively trapped by the olefin present in the reaction mixture. The effective concentration of each abstracting species, Br· or NS·, can therefore be controlled by the relative concentrations of the olefin and the benzene. The resultant effect of the competitive scavenging of the two radicals was to lower the yield of brominated cycloalkane, lower the yield of β-BPIC, and to give a variable value for k_5/k_6 (i.e., $k_5/k_6 = 1.3$)[3] depending upon the relative concentrations of the two scavengers; all of these effects were observed. In reaction mixtures of the proper relative concentration of reactants a mixed chain was ensured.

Two of the limiting conditions that have been proposed to enable one to observe the reaction of one of the two states of the succinimidyl radical, mixtures of NBS–Br_2 and mixtures of NBS–CCl_3Br, have now been reinvestigated. Both of these reagents are perported to limit the reactions of the substrates which do not react readily with bromine to the reaction of the π-succinimidyl radical and for the reactions of more reactive substrates, such as cyclohexane and cyclopentane, to π-succinimidyl and/or the bromine atom.[3,7d,e] With either class of substrate the major criteria which establishes the identity of the succinimidyl radical involved is that no ring-opened material, β-BPIC, should be observed in the reactions of π-succinimidyl. In our reactions with NBS–Br_2 ring-opened material is always found for the reactive substrates (this report and in our previous publication on this system[1]) and for the reagent NBS–CCl_3Br, the ring-opened material is only limited but not eliminated. The interpretation of these results is entirely consistent with the conclusions reached from an extensive study of the bromination of the nonreactive substrates, neopentane and methylene chloride, or mixtures of these substrates with added reactive substrates.[10,11] A full account of these latter studies will be reported elsewhere.[12]

Experimental Section

Proton NMR spectra were recorded by using a Bruker WH-200 200-MHz Fourier transform spectrometer with multiple solvent suppression (48 scans, 10-s relaxation delay between scans) or for the purpose of comparison a Varian EM-360 60-MHz spectrometer. Water determinations were obtained by using a Mitsubishi Moisturemeter MCI Model CA-02.

NBS (Fisher Scientific) was recrystallized from hot water and dried under vacuum over P_2O_5 for 48 h. Tritration showed it to be >99.5% pure. The NBS was sealed and stored in the dark (0 °C). The container was warmed to room temperature before opening.

Bromine (Fisher Scientific) was washed twice with concentrated sulfuric acid, decanted, and fractionally distilled (18-in. Vigreux column) from P_2O_5. The middle fraction was collected.

Vinylidene chloride (Aldrich) was distilled immediately before use.

Dichloromethane (Caledon Chemical Co.) was dried over sodium sulfate and distilled by using a 3-ft. Teflon spinning-band column. GLC analysis showed it to be >99.98% pure.

Cyclopentane (Aldrich) and cyclohexane (Phillips 66, research grade) were heated to reflux over P_2O_5 and fractionally distilled by using an 18-in. Vigreux column, and the middle fractions were collected. GLC analysis showed them to be >99.9% pure.

Bromotrichloromethane, benzene and carbon tetrachloride were distilled from P_2O_5 (18-in. Vigreux column). The middle fractions were collected. GLC analysis showed them to be >99% pure.

Di-*tert*-butyl peroxyoxalate was prepared by the method of Bartlett, Benzing, and Pincock[13] and used without further purification.

Photoinitiated Reactions of NBS. NBS was weighed into Pyrex reaction ampules which were protected from light. A solution of the substrates (cyclopentane and cyclohexane), the additives (bromine, vinylidene chloride and bromotrichloromethane, or vinylidene chloride and carbon tetrachloride), and the solvent (dichloromethane) was prepared and an aliquot added to each reaction ampule. The ampules were degassed by the freeze–thaw high vacuum technique (three cycles), sealed, equilibrated to 15 °C, and irradiated through three layers of Pyrex using a 275 watt sunlamp. At the appropriate time (4–24 h) the reaction was quenched by freezing (–190 °C) and the ampule was opened. An NMR standard, $CHBr_3$, was added, the sample was diluted with dichloromethane until all residual materials were soluble, and an aliquot was placed in an NMR tube for analysis of β-BPA, β-BPIC, and succinimide. The remaining solution was titrated iodometrically, the organic layer was separated, dried, and quantitatively analyzed for C_5H_9Br, $C_5H_8Br_2$, $C_6H_{11}Br$, *trans*-$C_6H_{10}Br_2$, $BrCH_2CCl_2Br$, $BrCHCl_2$, $CHCl_3$, and Cl_3C-CCl_3 by GLC analysis using a 50-m methylsilicone capillary column. The structure of the products of the reaction were assigned by a comparison of their GLC retention times, their mass spectrum, and IR spectrum (GLC) with those of authentic materials.

Thermally Initiated Reactions of NBS. NBS was weighed into Pyrex reaction ampules which were protected from light. A solution of the substrates (cyclopentane and cyclohexane), the additives (vinylidene chloride, benzene, and di-*tert*-butyl peroxyoxalate), and the solvent (dichloromethane) was prepared and an aliquot added to each reaction ampule. The ampules were degassed by the freeze–thaw high vacuum technique (three cycles), sealed, and equilibrated to 30 °C. At the appropriate time (4–24 h) the reaction was quenched by freezing (–198 °C) and the ampule was opened. The mixture was analyzed in the same manner as described for the photoinitiated experiments.

Analysis of β-BPA, β-BPIC, and Succinimide. An aliquot of deuteriodichloromethane (10–20% by volume to provide a lock signal) was added to the NMR sample, and the tube was sealed. The solvent and substrate signals were suppressed by irradiating at their frequencies of absorption to obtain an acceptable signal/noise ratio. A 10-s relaxation delay ($T_1 \approx 2.5$ s) was utilized, and 48 scans were collected by using the 200-MHz Fourier transform spectrometer described. The signal assignments and measurements were made as described previously.[1]

Analysis of H_2O Content. Dichloromethane was freshly distilled from P_2O_5 through an 18-in. Vigreux column. A sample was analyzed by using the moisture instrument described with a minimum exposure of the sample to air. The water content was found to be 1.7×10^{-3} M. A second sample was placed in a 0.5-mm path length IR solution cell with KCl windows (stored in a desiccator when not in use) and allowed to remain there for 10 min.

(8) Day, J. C.; Katsaros, M. G.; Kocher, W. D.; Scott, A. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950.
(9) Lu, F.; Naguib, Y. M. A.; Kitadani, M.; Chow, Y. L. *Can. J. Chem.* **1979**, *57*, 1967.
(10) Meintzer, C. P. Ph.D. Dissertation, University of Alberta, 1984.
(11) Presented in part at the 4th International Symposium on Organic Free Radicals, St. Andrews, Scotland, July 1984, abstracts, p 15.
(12) (a) Tanner, D. D.; Reed, D. W.; Tan, S. L.; Meintzer, C. P.; Walling, C.; Sopchik, A. *J. Am. Chem. Soc.*, in press. (b) Tanner, D. D.; Meintzer, C. P. *J. Am. Chem. Soc.*, in press.
(13) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

The sample was removed from the cell and analyzed for H_2O content 6.1×10^{-3} M). A sample of NBS (0.0866 g) was weighed into a Pyrex reaction ampule which was protected from light. An aliquot of the dichloromethane (2 mL) was added, and the vessel was attached to a high vacuum system. The volatile material was transferred under vacuum to a second vessel and was analyzed for its H_2O content and found to be 1.1×10^{-2} M.

Registry No. NBS, 128-08-5; cyclopentane, 287-92-3; cyclohexane, 110-82-7; succinimidyl radical, 24344-83-0.

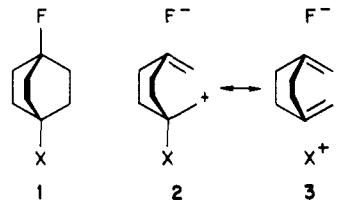
Fluorine-19 Nuclear Magnetic Resonance Studies of 4-Substituted Bicyclo[2.2.2]oct-1-yl Fluorides: Resonance Effects of Some Group 14 Substituents Attached to Saturated Carbon Centers†

William Adcock* and V. Sankar Iyer

School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia, Australia 5042

Received August 1, 1984

Recent studies[1,2] have revealed that the ^{19}F chemical shifts of 4-substituted bicyclo[2.2.2]oct-1-yl fluorides **1** respond sensitively and systematically to the polar electronic effects of remote substituents. The resulting ^{19}F



1 2 3

substituent chemical shifts (SCS), which reflect primarily changes in the fluorine σ-electron density,[1,3] are dominated by the polar field (σ_F effect) and electronegativity (σ_X effect) influences of the substituent. The former factor has its origin in the polarization of the CF σ bond and, thus, depends on the component of the electric field along the CF bond (E_z) as well as on the longitudinal polarizability of the CF bond. The latter substituent factor, which pertains to the polarity of the substituent–substrate bond (σ-inductive effect), is transmitted chiefly by a "through-three-bond" electron delocalization mechanism (a σ-resonance or $\sigma-\sigma$ hyperconjugative effect.[4] In valence bond terminology, the σ-resonance effect in **1** may be denoted by canonical structures **2** and **3** (depicted for only one of the three ethano bonds). Thus, the dependence of the ^{19}F SCS of **1** on substituent electronegativity may be understood on the basis of the relative importance of these contributing resonance canonical structures. It should be noted that these structures are analogous to the resonance structures commonly drawn to represent hyperconjugative interactions ($\sigma-\pi$) between the C–F bond (and C–X bond) and the π-system in CH_2X derivatives of benzyl fluoride. Within the framework of PMO theory,[5] the resonance effect in **1** is proportional to $c^2\beta^2/\Delta E$, where c is the coefficient at the carbon atom of attachment (or site of substitution), β is the resonance integral associated with the appropriate orbitals, and ΔE is the orbital energy gap between the orbitals. The former parameter dominates the numerator of the expression for three-center donor–acceptor orbital interactions of the type C···C–X.[6] Hence, an alternative means of rationalizing the aforementioned electronegativity effect in **1** centers around the magnitude of c and ΔE for the appropriate bond MOs (σ_{CX} and σ_{CX}^*).[6]

Table I. ^{19}F Substituent Chemical Shifts (SCS)[a] of System 1 for Some Group 14 Substituents: Polar Field ($\rho_F\sigma_F$)[b,c] and Electronegativity ($\rho_X\sigma_X$)[d] or Resonance Contributions

	SCS, ppm		$\rho_F\sigma_F$, ppm		$\rho_X\sigma_X$, ppm	
	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$	c-C_6H_{12}	$CDCl_3$
CMe_3	−3.11[e]	−3.20[e]	−0.03	−0.11	−3.08	−3.09
$SiMe_3$[f]	1.54	1.61	0.00	−0.05	1.54	1.66
$GeMe_3$	1.63	1.69	−0.03	−0.11	1.66	1.80
$SnMe_3$	3.67[e]	3.83[e]	−0.03	−0.11	3.70	3.94
$PbMe_3$[g]	2.87	3.00	−0.16	−0.26	3.03	3.26

[a] Chemical shifts (ppm) relative to parent system (1, X = H). A positive sign implies deshielding (downfield shift). Accurate to ±0.01 ppm. [b] ρ_F values for system 1 in c-C_6H_{12} and $CDCl_3$ are −3.13 and −5.25, respectively (see ref 1). [c] σ_F values derived from the ^{19}F SCS of 1-X-4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes (ρ_F values for c-C_6H_{12} and $CDCl_3$ are 2.70 and 2.57, respectively (see ref 1)). ^{19}F SCS of this system in c-C_6H_{12} for MMe_3 groups (see ref 9b) lead to the following σ_F parameters: 0.01 (CMe_3), 0.00 ($SiMe_3$), 0.01 ($GeMe_3$), 0.01 ($SnMe_3$), 0.05 ($PbMe_3$). ^{19}F SCS (ppm) for $CDCl_3$ (this study) are as follows: 0.05 (CMe_3), 0.03 ($SiMe_3$), 0.06 ($GeMe_3$), 0.04 ($SnMe_3$), 0.14 ($PbMe_3$). These SCS lead to similar σ_F values: 0.02 (CMe_3), 0.01 ($SiMe_3$), 0.02 ($GeMe_3$), 0.02 ($SnMe_3$), 0.05 ($PbMe_3$). [d] ^{19}F SCS (obsd) $-\rho_F\sigma_F$ (ppm). [e] Taken from ref 1. [f] $J_{^{29}Si-^{19}F}$ not observed. [g] $J_{^{207}Pb-^{19}F}$ values (Hz): 134.5 (c-C_6H_{12}), 143.8 ($CDCl_3$).

† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Adcock, W.; Abeywickrema, A. N. *Tetrahedron Lett.* **1981**, *22*, 1135. Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2957.

(2) Adcock, W.; Abeywickrema, A. N.; Kok, G. B. *Tetrahedron Lett.* **1982**, *23*, 3615. Adcock, W.; Abeywickrema, A. N.; Kok, G. B. *J. Org. Chem.* **1984**, *49*, 1387.

(3) (a) A *decrease* in σ-electron density leads to *negative* ^{19}F SCS (*upfield* shift) in system 1.[3b] The converse situation holds for an *increase* in σ-electron density.[3c] (b) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 2945. (c) On the basis of theoretical studies, it has been suggested that an *increase* in the total electronic population is accompanied by a downfield shift (sp^3C, carbonyl C, and dialkyl ether O atoms) when the increase in charge is dictated by that of the σ population (Fliszár, S.; Cardinal, G.; Béraldin, M. T. *J. Am. Chem. Soc.* **1982**, *104*, 5287).

(4) (a) We have proposed[1,2] that the electronegativity dependent "through-three-bond" effect (TB-3 effect) in **1** is governed predominantly by the hyperconjugative interaction between the bridging ethano bonds and the C–F bond, i.e., $\sigma_{CC}-\sigma_{CF}^*$, the dominant donor–acceptor interaction (represented in valence bond terms by structure **2**). This conjugative interaction may be enhanced or decreased (relative to X = H) depending on the net result of the hyperconjugative interactions between σ_{CC} and the substrate–substituent bond molecular orbitals (σ_{CX} and σ_{CX}^*). (b) It is of interest to note that Grob et al.[4c] have invoked a similar resonance effect (called twofold hyperconjugation) to account for the fact that certain 4-substituted (X) bicyclo[2.2.2]octyl nisylates (X = H, COO^-, $CONH_2$, CH_2OH, and CH_2NH_2) appear to solvolyze faster than expectations based on σ_I^q values (derived from the pK_a values of 4-substituted quinuclidium perchlorates). Subsequently, calculations were presented[4d] which did not support the concept. However, odd electron delocalization onto the remote C–H bond in the bicyclo[2.2.2]octan-1-yl radical[4e] is further strong experimental evidence for the resonance idea. It is important to bear in mind that, in general, "through-bond" effects cannot compete with direct polar field interactions ($\rho_F\sigma_F$) in the case of chemical reactivity.[2] (c) Grob, C. A.; Rich, R. *Tetrahedron Lett.* **1978**, 663. Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793. (d) Wenke, G.; Lenoir, D. *Tetrahedron Lett.* **1979**, 2823. (e) Kawamura, T.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 92 and references cited therein.

(5) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975.

(6) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.

0022-3263/85/1950-1538$01.50/0