Photochemistry of Alkyl Halides. 4. 1-Norbornyl, 1-Norbornylmethyl, 1- and 2-Adamantyl, and 1-Octyl Bromides and Iodides[1]

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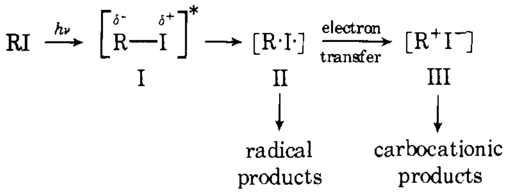
Abstract: Competing ionic and radical photobehavior has been observed for a number of alkyl halides. Irradiation of 1-iodonorbornane (**1a**) in a variety of media afforded predominantly the nucleophilic substitution product **3** or **6**, accompanied by lesser amounts of the reduction product norbornane (**8**). The bromo analogue **1b** exhibited similar behavior except that a higher proportion of the reduction product norbornane (**8**) was formed. The 1- and 2-haloadamantanes **10** and **13** similarly afforded a mixture of adamantane (**11**) and the nucleophilic substitution products **12** or **14**, with the iodides generally affording a higher proportion of the latter products than the bromides. 1-Iodomethylnorbornane (**15a**) afforded principally the rearranged products **18** and **19**, whereas the bromo analogue **15b** gave predominantly the reduction product 1-methylnorbornane (**20**). 1-Iodooctane (**22a**) afforded mainly 1-octene (**26**), accompanied by octane (**24**) and a mixture of 2- and 3-octene (**27**). Both 1- and 2-octyl substitution products (**28** and **29**) were also formed in low yields. By contrast, 1-bromooctane (**22b**) afforded almost exclusively the reduction product octane (**24**). The use of ethylene glycol resulted in increased yields of ionic products from iodides **1a**, **10a**, **13a**, and **22a**, whereas the presence of triethylamine resulted in enhanced yields of the reduction products from iodides **1a** and **22a**. Irradiation of 1-iodonorbornane (**1a**) in methanol saturated with oxygen, followed by reductive workup with sodium borohydride, afforded 1-norbornanol (**6**) as the principal photoproduct. The quantum yield for disappearance of **1a** increased on changing the atmosphere from nitrogen to air and, finally, to oxygen. Irradiation of 1-iodo- and 1-bromonorbornane (**1a** and **b**) in methanol-*O-d* afforded the ether **3a** with no detectable incorporation of deuterium. Likewise, there was no significant incorporation of deuterium in the rearranged ethers **18a** and **19a** obtained from irradiation of 1-iodomethylnorbornane (**15a**) in methanol-*O-d*. The results are discussed in terms of initial homolytic cleavage of the carbon–halogen bond to afford a radical pair (II), which undergoes competing (a) diffusion and hydrogen abstraction to give reduction products and (b) electron transfer to afford an ion pair (III). The ion pair, in turn, gives rise ultimately to the substitution and elimination products.

The photochemistry of alkyl halides has been the object of extensive study over the years and the subject of several recent reviews.[3,4] The earlier studies were conducted mainly in the gas phase,[3] but some reports of photobehavior in the liquid or solution phase have also appeared.[4] In all of these studies the common theme has been the formation of radical products resulting from initial homolytic cleavage of the carbon-halogen bond.[3-5] We wish now to report results which clearly show that in solution the initially generated radical pair (II) can undergo subsequent electron transfer to afford an ion pair (III) and, ultimately, carbocationic products (Scheme I).

Scheme I



Indeed, the photochemistry of alkyl halides is a convenient means for the generation of carbocations, especially those of high energy.[8]

Results

Five alkyl halide systems were selected for study on the basis of specific insights which the photobehavior of each would provide: the 1-norbornyl, 1- and 2-adamantyl, 1-norbornylmethyl, and 1-octyl. The results from irradiation of the bromides and iodides of these systems in a variety of media are summarized in the tables below. Except where indicated, there was no detectable reaction in the absence of light. The photoproducts were identified on the basis of spectral data and by comparison with independently prepared specimens as outlined in the Experimental Section.

Alkyl iodides have a low-lying n → σ^* transition with $\lambda_{max} \sim 260$ nm.[9] It was thus convenient to conduct irradiations of iodides with a low-pressure mercury lamp, which has its principal emission at 254 nm. However, since absorption is substantially blue shifted in alkyl bromides ($\lambda_{max} \sim 210$ nm), the broad spectral emission of a medium-pressure arc had to be employed with these compounds. Several comparison studies revealed similar behavior by iodides **1a** and **15a** on irradiation with either a low- or medium-pressure lamp.

1-Halonorbornanes (1a and b). The photochemical behavior of 1-iodonorbornane (**1a**) in a variety of media is summarized in Table I and Scheme II. Only two photoproducts could be

Scheme II

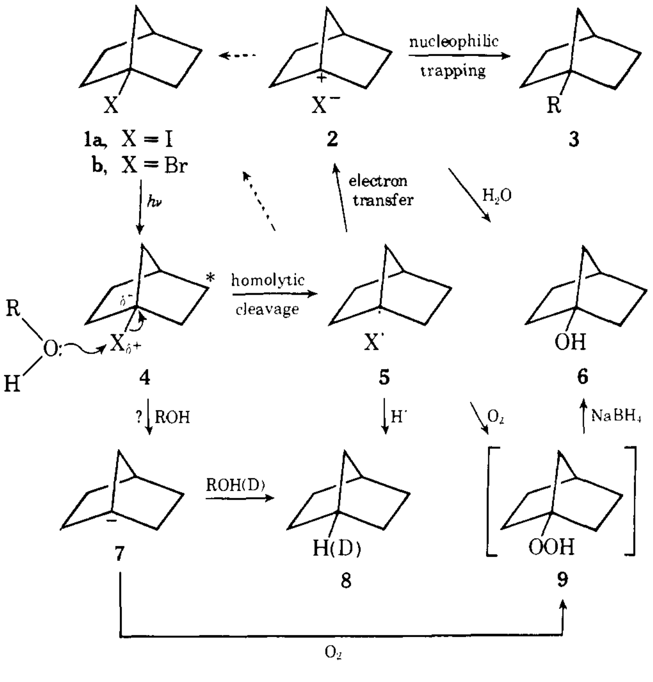


Table I. Irradiation of 1-Iodo- and 1-Bromonorbornane (1a and b)[a]

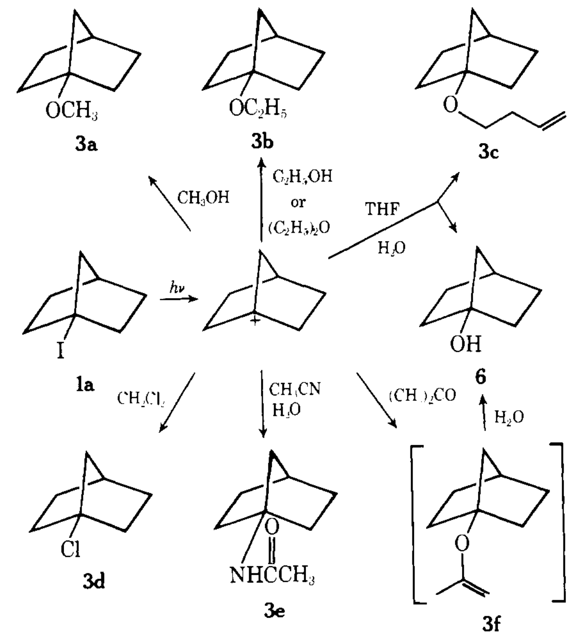
Halide	Solvent	Time, h	Yield, %[b] 1	3	6	8	R
1a	CH_3OH	2	4	76		12	OCH_3
1a	aq CH_3OH[d]	2	*c*	60	22	3	OCH_3
1a	CH_3OH[e]	2	11	41	47	*f*	OCH_3
1a	CH_3OH[g]	6	*c*	52		43	OCH_3
1a	CH_3OH[h]	2	3	72		15	OCH_3
1a	CH_3OH[d,h]	2	*c*	79	*f*	7	OCH_3
1b	CH_3OH[h]	8	3	30		55	OCH_3
1b	CH_3OH[h,i]	8	13	41		44	OCH_3
1b	CH_3OH[h,e]	8	10	19	40	30	OCH_3
1a	$(C_2H_5)_2O$	4	18	63		19	OCH_2CH_3
1a	$(C_2H_5)_2O$[d]	4	4	58		22	OCH_2CH_3
1a	$(C_2H_5)_2O$[h]	4	5	55		23	OCH_2CH_3
1a	$(C_2H_5)_2O$[d,h]	4	2	63		16	OCH_2CH_3
1a	C_2H_5OH	4	4	58		22	OCH_2CH_3
1b	$(C_2H_5)_2O$	24	66	7		17	OCH_2CH_3
1b	$(C_2H_5)_2O$[i]	24	48[j]	23		13	OCH_2CH_3
1a	THF	8	*c*	60		15	$OCH_2CH_2CH{=}CH_2$
1a	THF[d]	8	*c*	33	19	6	$OCH_2CH_2CH{=}CH_2$
1a	THF[h]	8	*c*	54		20	$OCH_2CH_2CH{=}CH_2$
1a	33% aq THF[k]	20	*c*	28	66	4	$OCH_2CH_2CH{=}CH_2$
1a	CH_3CN	4	5	56		10	$NHCOCH_3$
1a	CH_3CN[d]	4	4	54		5	$NHCOCH_3$
1a	CH_3CN[h]	4	*c*	9		16	$NHCOCH_3$
1a	CH_2Cl_2	4	4	86			Cl
1a	$(CH_3)_3COH$	12	3	21	46	11	$OC(CH_3)_3$
1b	$(CH_3)_3COH$	24	31	4	34	28	$OC(CH_3)_3$
1a	$(CH_2OH)_2$[l]	8	*f*	99		*e*	$O(CH_2)_2OH$
1b	$(CH_2OH)_2$[l]	16	*f*	92	10	6	$O(CH_2)_2OH$
1a	CH_3COCH_3	12	52		36	11	
1a	CH_3COCH_3[m]	12	20		58	19	
1a	CH_3COCH_3[g]	12	5		36	57	
1a	C_6H_6	8	12	86			C_6H_5
1a	$C_6H_5CH_3$	16	23	43[n]			$C_6H_4CH_3$

[a] Irradiations were conducted at 254 nm as described in the Experimental Section in quartz tubes using 5-ml solutions containing 100 mg of halide. Unless otherwise stated, all irradiations were carried out under a nitrogen atmosphere. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] None detectable. [d] Carried out under an air atmosphere. [e] Solution saturated with oxygen; reductive workup using sodium borohydride. [f] Trace. [g] Triethylamine (1 mol equiv) present. [h] The broad emission of a 450-W medium-pressure mercury arc was employed. [i] An equimolar amount of I_2 was added. [j] Iodide 1a (8%) was also detected. [k] Preparative run; conducted in quartz flask using 100 ml of tetrahydrofuran containing 2 g of iodide. [l] Conducted using 10 ml of solvent. [m] Zinc metal present. [n] 22% ortho, 12% meta, and 9% para.

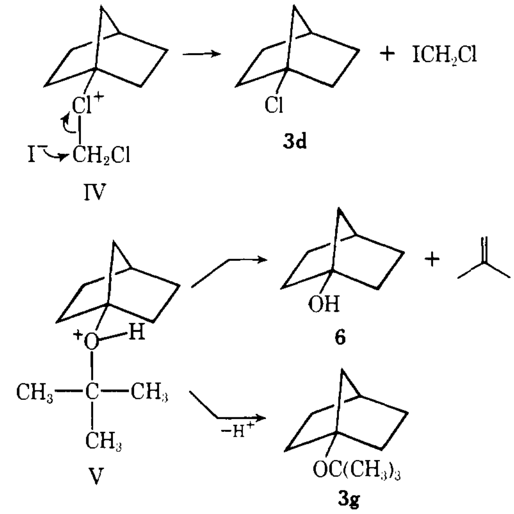
detected: a substitution product **3** or **6**, accompanied by a small amount of the reduction product norbornane (**8**). This latter product apparently arises at least principally via the 1-norbornyl radical. On the other hand, the major photoproduct **3** or **6** clearly arises from nucleophilic trapping of the 1-norbornyl cation. Indeed, irradiation of iodide **1a** represents a particularly convenient method for generating this high energy cation, which is not easily prepared by conventional methods,[10] in high chemical yield, in a variety of media, and at almost any desired temperature. The contrasting reluctance of iodide **1a** to undergo ionic cleavage under nonphotochemical conditions was emphasized by its quantitative recovery from extended treatment with refluxing methanolic silver nitrate.

Irradiation of **1a** afforded an opportunity to explore the behavior of the unusually reactive 1-norbornyl cation (Scheme III). In methanol or ethanol the ether **3a** or **b** was obtained, respectively. The latter product was also obtained in ether solution and the butenyl ether **3c** was formed in tetrahydrofuran;[11] in aqueous tetrahydrofuran the alcohol **6** was also obtained. In methylene chloride abstraction of chlorine occurred to give **3d**, presumably via attack of iodide ion on the initially formed intermediate IV[11] (Scheme IV), and in acetonitrile containing traces of water the amide **3e** was formed. Irradiation in anhydrous acetone afforded a product, thought to be the enol ether **3f**, which could not be fully characterized because of its facile hydrolysis to alcohol **6**. Indeed, irradiation of **1a** in acetone followed by aqueous workup proved to be a method of choice for preparing alcohol **6**. Reaction was observed with essentially every solvent investigated except for saturated hydrocarbons. Trapping occurred even with the highly hindered *tert*-butyl alcohol, except that in this case the initially formed intermediate V principally underwent fragmentation to the alcohol **6** and isobutylene, along with some

Scheme III



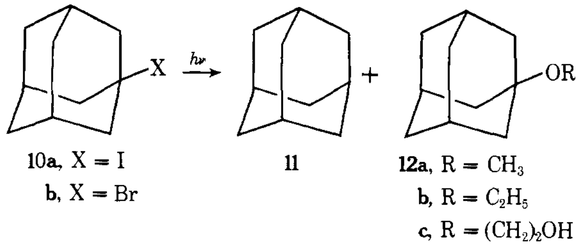
Scheme IV



deprotonation to form the *tert*-butyl ether **3g**. Thus the 1-norbornyl cation is a sufficiently strong acid to cleave ethers and methylene chloride and to dehydrate *tert*-butyl alcohol.

No significant differences were noted between irradiation of **1a** at 254 nm or with the broad spectral emission of a 450-W medium-pressure mercury arc except for a substantial decrease in the yield of amide **3e** in acetonitrile. It is likely that amide **3e** is photolabile at the shorter wavelengths present in the broad spectrum. In some cases it was found that the use of zinc as a scavenger for iodine in irradiations of **1a** led to faster rates of conversion. However, there were no significant differences in the course of reaction with or without zinc present.

Products from trapping of the 1-norbornyl cation were also obtained on irradiation of the bromide **1b** in a variety of media. However, as shown in Table I, the ratio of these products to the reduction product norbornane (**8**) was substantially lower than that obtained from irradiation of the iodide and, indeed, **8** was usually the major photoproduct from the bromide. The addition of an equimolar amount of iodine during irradiation of bromide **1b** in methanol or ether resulted in a slight increase in the amount of substitution product **3a** or **b** formed. This increase was at least partly due to formation and subsequent photolysis of iodide **1a**, since its presence could be detected during the irradiation. The chloride **3d** has only weak absorption above 200 nm (ϵ 13 at 201 nm in ethanol) and was photostable under the irradiation conditions.



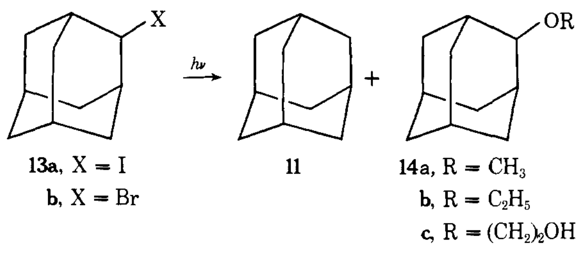


Table II. Irradiation of 1-Iodo- and 1-Bromoadamantane (10a and b)[a]

		Time,	Yield, %[b]			
Halide	Solvent	h	10	11	12	R
10a	CH$_3$OH	24	4	*c*	95	CH$_3$
10a	CH$_3$OH[d]	24	*c*	*c*	90[e]	CH$_3$
10b	CH$_3$OH	48	10	13	48	CH$_3$
10a	(C$_2$H$_5$)$_2$O	24	80	12	4	C$_2$H$_5$
10b	(C$_2$H$_5$)$_2$O	32	*f*	68	8	C$_2$H$_5$
10a	(CH$_2$OH)$_2$[g]	24	*f*	*c*	98	(CH$_2$)$_2$OH
10b	(CH$_2$OH)$_2$[g]	24	*f*	6	83	(CH$_2$)$_2$OH

[a] Unless otherwise stated, irradiations were conducted as described in the Experimental Section under nitrogen atmosphere using either 100-ml solutions containing 2.0 g of bromide 10b and employing the broad emission of a 450-W medium-pressure arc or at 254 nm using 50-ml solutions in quartz flasks containing 1.0 g of iodide **10a**. Zinc was not used. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] None detectable. [d] Solution saturated with oxygen; reductive workup using sodium borohydride. [e] 1-Adamantanol also formed (10% yield). [f] Trace. [g] Conducted using 1.0 g of halide dissolved in 100 ml of ethylene glycol and 15 ml of diglyme.

Table III. Control Runs for 1-Iodo- and 1-Bromoadamantane (**10**a and b)[a]

		Time,	Yield, %[b]			
Halide	Conditions	h	10	11	12	R
10a	CH$_3$OH, 41 °C	24	93	*c*	7	CH$_3$
10b	CH$_3$OH, 55 °C	48	86	*c*	14	CH$_3$
10a	(C$_2$H$_5$)$_2$O, 41 °C	24	100	*c*	*c*	
10b	(C$_2$H$_5$)$_2$O, reflux	36	100	*c*	*c*	
10a	(CH$_2$OH)$_2$, 41 °C[d]	24	39	*c*	61	(CH$_2$)$_2$OH
10b	(CH$_2$OH)$_2$, 55 °C[d]	24	72	*c*	28	(CH$_2$)$_2$OH
10a	CH$_3$OH, AgClO$_4$[e]	0.2	36	*c*	64	CH$_3$

[a] Conducted as described in the Experimental Section at the indicated temperature using 5-ml solutions in covered Pyrex vessels containing 100 mg of halide. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] None detectable. [d] Conducted using 100 mg of halide dissolved in 10 ml of ethylene glycol and 2 ml of diglyme. [e] Approximately 2 mol equiv of silver perchlorate present at room temperature.

Table IV. Irradiation of 2-Iodo- and 2-Bromoadamantane (13a and b)[a]

		Time,	Yield, %[b]			
Halide	Solvent	h	13	11	14	R
13a	CH$_3$OH	24	5	1	91	CH$_3$
13b	CH$_3$OH	48	2	19	47	CH$_3$
13a	(C$_2$H$_5$)$_2$O	24	30	6	63	C$_2$H$_5$
13b	(C$_2$H$_5$)$_2$O	32	46	38	3	C$_2$H$_5$
13a	(CH$_2$OH)$_2$[c]	24	*d*	*e*	96	(CH$_2$)$_2$OH
13b	(CH$_2$OH)$_2$[c]	24	9	6	74	(CH$_2$)$_2$OH

[a] Irradiations were conducted as described in the Experimental Section under a nitrogen atmosphere using either 100-ml solutions containing 2.0 g of bromide 13b and employing the broad emission of a 450-W medium-pressure arc or at 254 nm using 50-ml solutions in quartz flasks containing 1.0 g of the iodide 13a. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Conducted using 1.0 g of halide dissolved in 100 ml of ethylene glycol and 15 ml of diglyme. [d] None detectable. [e] Trace.

1- and 2-Haloadamantanes (10 and 13). The formation of photoproducts clearly derived from nucleophilic trapping of carbocations is not restricted to 1-iodonorbornane (**1a**). Similar behavior was found for 1- and 2-iodoadamantane (**10a** and **13a**), which, as outlined in Tables II and IV, afforded principally the methyl ethers **12a** and **14a** on irradiation in methanol.[12] The 2-isomer **13a** likewise afforded principally the ethyl ether **14b** on irradiation in ether, accompanied by a minor amount of the reduction product adamantane (**11**). However, the 1-isomer **10a** underwent only slow conversion under similar conditions to afford small amounts of adamantane and the

Table V. Control Runs for 2-Iodo- and 2-Bromoadamantane (**13a** and b)[a]

Halide	Conditions	Time, h	Yield, %[b] **13**	**11**	**14**	R
13a	CH_3OH, 41 °C	24	96	*c*	3	CH_3
13b	CH_3OH, 55 °C	48	93	*c*	5	CH_3
13a	$(C_2H_5)_2O$, 41 °C	24	97	*c*	*c*	
13b	$(C_2H_5)_2O$, 55 °C	32	100	*c*	*c*	
13a	$(CH_2OH)_2$, 41 °C[d]	24	93	*c*	7	$(CH_2)_2OH$
13b	$(CH_2OH)_2$, 55 °C[e]	24	91	*c*	9	$(CH_2)_2OH$
13b	CH_3OH, $AgClO_4$[f]	0.2	19	*c*	78	CH_3

[a] Conducted as described in the Experimental Section at the temperature indicated using 5-ml solutions in covered Pyrex vessels containing 100 mg of halide. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] None detectable. [d] Conducted using 100 mg of **13a** dissolved in 10 ml of ethylene glycol and 2 ml of diglyme. [e] Conducted using 100 mg of **13b** dissolved in 10 ml of ethylene glycol and 3 ml of diglyme. [f] A 1.0 mol equiv of silver perchlorate was added and the reaction was run at room temperature.

Table VI. Irradiation of 1-Iodomethyl- and 2-Bromomethylnorbornane (**15a** and b)[a]

Halide	Solvent	Time, h	Yield, %[b] **15**	**18**	**19**	**20**	R
15a	CH_3OH	6	*c*	37	47	*c*	OCH_3
15b	CH_3OH[d]	8	47	6	6	14	OCH_3
15a	$(C_2H_5)_2O$	6	*c*	28	38	*c*	OC_2H_5
15a	C_6H_6[e]	18	15	37	43		C_6H_5
15a	C_5H_{12}[f,g]	2	41	16	2		I
		6	16	14	4		I
15b	C_5H_{12}	36	38			56	

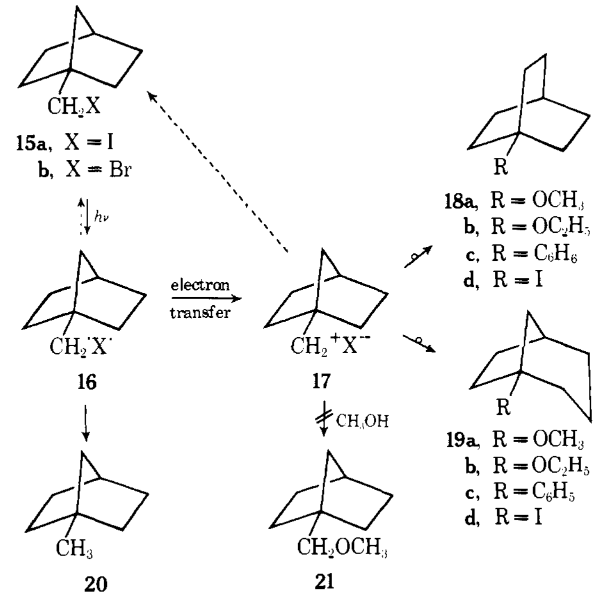
[a] Irradiations were conducted at 254 nm as described in the Experimental Section under a nitrogen atmosphere using 5-ml solutions in a quartz tube containing 100 mg of **15a**. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. [c] Trace. [d] Conducted using 55 mg of **15b** and the broad emission of a 450-W mercury arc. [e] Conducted using 235 mg of **15a** in 10 ml of benzene. [f] An unidentified iodide was also obtained in 6–7% yield. [g] See ref 13.

ethyl ether **12b**. This difference in behavior is probably attributable to the greater stability of the 1-adamantyl cation, which renders nucleophilic trapping by ether less efficient. In the absence of trapping of the carbocation by solvent, internal return within the ion pair probably occurs to regenerate the starting iodide **10a**.

Similar behavior was exhibited by the bromo analogues **10b** and **13b** except that, once again, the proportion of reduction product **11** was higher than for the corresponding iodides. The greater solvolytic reactivities of the 1- and 2-adamantyl halides afforded some competing ground-state reaction. However, as outlined in Tables III and V, control runs showed clearly that reaction was greatly enhanced in the presence of ultraviolet light. Because of competing ground-state reactions zinc could not be used as an iodine scavenger in irradiations of the haloadamantanes.

1-Halomethylnorbornanes (15a and b). Further insight was gained by a study of halides **15**, the results of which are summarized in Table VI. Irradiation of the iodide **15a** in methanol afforded a mixture of the rearranged bicyclo[2.2.2]- and bicyclo[3.2.1]octyl ethers **18a** and **19a**, with the latter predominating (Scheme V). There was no detectable formation of the unrearranged ether **21**. No reaction was observed in the absence of light. Silver ion assisted methanolysis afforded, by contrast, principally the bicyclo[2.2.2]octyl ether **18a** (76%), accompanied by lesser amounts of both the unrearranged ether **21** (15%) and the bicyclo[3.2.1]octyl ether **19a** (8%).

Scheme V



Irradiation of **15a** in ether solution afforded the ethyl ethers **18b** and **19b**; the analogous phenyl derivatives **18c** and **19c** were obtained in benzene. Thus the 1-bicyclo[2.2.2]- and 1-bicyclo[3.2.1]octyl bridgehead cations are apparently sufficiently reactive to undergo electrophilic trapping by ether and benzene. In no case were more than trace amounts of the reduction product 1-methylnorbornane (**20**) observed. By contrast, irradiation of the bromide **15b** in methanol afforded **20** as the principal photoproduct, accompanied by small amounts of ethers **18a** and **19a**. Irradiation of iodide **15a** in pentane, conditions under which there was no available nucleophile other than iodide ion, resulted in isomerization to the 1-bicyclo[2.2.2]- and 1-bicyclo[3.2.1]octyl iodides **18d** and **19d**.[13] Once again the bromide afforded principally the reduction product **20** under similar conditions.

1-Halooctanes (22a and b). For comparison the behavior of a simple acyclic system was investigated; some important differences were observed (Scheme VI). As shown in Table VII, irradiation of the iodide **22a** in methanol, ether, or benzene afforded predominantly 1-octene (**26**), accompanied by octane (**24**) and a mixture of 2- and 3-octene (**27**).[14] Nucleophilic substitution products were found only in low yields, but, interestingly, usually included both 1- and 2-octyl derivatives. There was no reaction in the absence of light. However, methanolysis of **22a** at elevated temperature or in the presence of silver perchlorate afforded, by contrast, exclusively the 1-octyl ether (**28a**). Once again the bromide gave almost exclusively the reduction product octane (**24**) on irradiation.

Scheme VI

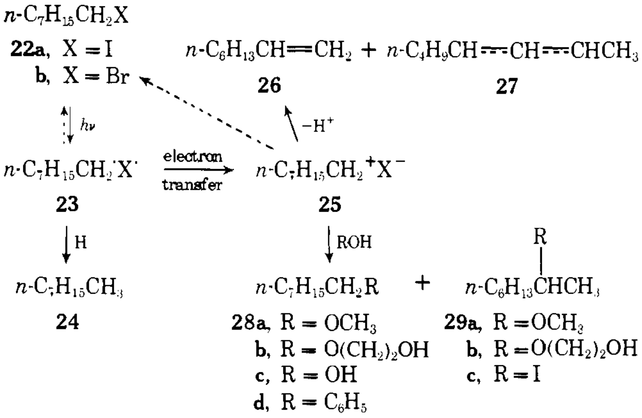


Table VII. Irradiation of 1-Iodo- and 1-Bromooctane (**22a** and b)[a]

Halide	Solvent	Time, h	Yield, %[b] 22	24	26	27	28	29	R
22a	CH_3OH	8	*c*	38	56	6	*d*	*c*	CH_3
22a	CH_3OH^f	8	31	8	40	5	4[g]	1[h]	CH_3
22a	CH_3OH^i	8	*d*	66	31	4	*d*	*d*	
22b	CH_3OH^e	24	18	68	*d*	*d*	*d*	*d*	
22a	$(C_2H_5)_2O$	8	2	18	65	9	*d*	*c*	
22a	$(C_2H_5)_2O^e$	12	*c*	23	58	9	*d*	*d*	
22b	$(C_2H_5)_2O^e$	33	8	70	*d*	*d*	*d*	*d*	
22a	CH_3CN	8	*c*	59	36	5	*d*	*d*	
22a	$(CH_3)_3COH$	12	*c*	28	55	16	*d*	*d*	
22a	$(CH_3)_3COH^i$	12	*c*	41	48	10	*d*	*d*	
22b	$(CH_3)_3COH^e$	24	27	33	2	*k*	*d*	*d*	
22a	$(CH_2OH)_2^j$	12	*c*	*c*	74	12	4	9	$(CH_2)_2OH$
22a	$(CH_2OH)_2^{i,j}$	12	26	48	19	3	1	2	$(CH_2)_2OH$
22a	C_6H_6	24	*c*	34	23	4	8	*d,l*	C_6H_5
22a	$C_6H_6^i$	24	*d*	*d*	78	5	7	*c*	C_6H_5

[a] Unless otherwise stated, the irradiations were conducted under nitrogen atmosphere at 254 nm in quartz flasks using 50-ml solutions containing 1.0 g of iodide. A small amount of zinc was employed in all irradiations of **22a**. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. The relative yield of olefins **26** and **27** was determined by NMR using concentrated reaction mixtures. [c] Trace. [d] None detectable. [e] The broad spectrum of a 450-W medium-pressure mercury arc was employed, using a 100-ml solution containing 2.0 g of halide. [f] Solution saturated with oxygen; reductive workup with sodium borohydride. [g] **28c** (7%) also formed. [h] **29c** (3%) also observed. [i] Triethylamine (1 mol equiv) added. [j] Carried out with 1.0 g of halide dissolved in 200 ml of ethylene glycol and 15 ml of diglyme. [k] Not determined. [l] **29c** (17%) also obtained.

Table VIII. Quantum Yield Determinations for Irradiations of 1-Iodonorbornane (**1a**) in Methanol

	ϕ		
	Disappearance	Appearance	
Atmosphere	**1a**	**3a**	**8**
Nitrogen	0.095	0.076	0.019
Air	0.11	0.064	0.005
Oxygen	0.13	0.059	0.004

Table IX. Irradiation of 1-Halonorbornanes **1a** and b in Methanol-*O*-*d*[a]

Halide	Time, h	Yield, %[b] 3a	8
1a	2	64	32
		D_1 0	D_1 13[c]
		D_0 100	D_0 87
1a[d]	2	89	11
		D_1 0	D_1 30
		D_0 100	D_0 70
1a[e]	6	52	43
		D_1 0	D_1 0
		D_0 100	D_0 100
1b[d]	8	33	48
		D_1 0	D_1 18
		D_0 100	D_0 82

[a] Unless otherwise indicated irradiations were conducted at 254 nm as described in the Experimental Section using 5-ml solutions containing 100 mg of halide. [b] Yields were determined by gas chromatographic analysis relative to an internal hydrocarbon standard and isotopic compositions were determined by mass spectral analysis. [c] Deuterium analysis for norbornane (**8**) obtained on material isolated from a similar run conducted using 500 mg of iodide in 25 ml of methanol-*O*-*d*. [d] The broad emission of a 450-W medium-pressure mercury arc was employed. [e] Triethylamine (1 mol equiv) present.

Solvent Effect. In each of the above examples irradiation of the iodide afforded predominantly the substitution or elimination product, usually accompanied by small amounts of the reduction product. The corresponding bromide gave substantially greater amounts of the reduction product, sometimes to the exclusion of any substitution product. There was relatively little dependency of product ratios on solvent polarity; for example, similar results were obtained in methanol and ether. However, a marked effect was noted on going to ethylene glycol, with a substantial increase in the amount of substitution product. Thus, irradiation of 1-iodonorbornane (**1a**) in ethylene glycol afforded the ether **3** (R = OCH_2CH_2OH) almost exclusively. Similar trends were observed for the haloadamantanes **10** and **13.** In the case of 1-iodooctane (**22a**) the use of ethylene glycol resulted in increased yields of the octenes **26** and **27** and the formation of the 1- and 2-octyl ethers **28b** and **29b.**

Effect of Triethylamine. Irradiation of either 1-iodonorbornane (**1a**) or 1-iodooctane (**22a**) in the presence of 1 mol equiv of triethylamine in a variety of solvents resulted in a marked increase in the relative amount of the reduction product norbornane (**8**) or *n*-octane (**24**) formed. The one exception to this was irradiation of **22a** in benzene, in which case there was a marked increase in the amount of 1-octene (**26**) at the apparent expense of the reduction product *n*-octane (**24**).

Effect of Oxygen. Irradiation of either 1-iodo- or 1-bromonorbornane (**1a** or **b**) in a methanolic solution saturated with oxygen resulted in substantially lower yields of both the substitution product **3a** and the reduction product **8** compared with irradiations conducted in the absence of oxygen. Reductive workup of the irradiation mixture using sodium borohydride afforded the alcohol **6** as the principal photoproduct.

Quantum Yields. As outlined in Table VIII, the quantum yields for the conversion of 1-iodonorbornane (**1a**) to the ether **3a** and norbornane (**8**) in methanol at 254 nm were determined in nitrogen, air, and oxygen atmospheres. The benzene-sensitized cis ⇄ trans isomerization of *trans*-2-octene was employed for actinometry.[15] Irradiations were conducted to 5–10% conversion; the rate of conversion was linear with time at these levels, but became nonlinear at higher levels of conversion. The combined quantum yields for appearance of products **3a** and **8** was 0.095 in a nitrogen atmosphere and was progressively lowered on going to air and then to oxygen. The quantum yield for disappearance of the iodide, however, increased as the atmosphere was changed from nitrogen to air and then to oxygen.

Deuterium Incorporation. The results from irradiation of the 1-halonorbornanes **1a** and **b** in methanol-*O*-*d* are summarized in Table IX. There was no detectable incorporation of deuterium in the ether **3a;** on the other hand, the reduction product norbornane (**8**) was formed with partial incorporation of deuterium. The location of deuterium incorporation was at least principally one of the bridgehead positions, as evidenced by a corresponding decrease in the integration for the band at τ 7.79 in the NMR spectrum of material obtained from irradiation of **1a** at 254 nm. By contrast, in the presence of 1 mol equiv of triethylamine, norbornane (**8**) was formed from **1a** with no detectable incorporation of deuterium. Irradiation of 1-iodomethylnorbornane (**15a**) in methanol-*O*-*d* afforded the rearranged ethers **18a** and **19a** with no significant incorporation of deuterium (Table X).

Sensitization. Irradiation of 1-iodonorbornane (**1a**) at 254 nm in benzene solution afforded 1-phenylnorbornane (**3**, R = C_6H_5); in toluene a mixture of *o*-, *m*-, and *p*-tolyl analogues **3** (R = $CH_3C_6H_4$) was obtained (Table I). Irradiation of 1-iodomethylnorbornane (**15a**) in benzene afforded a mixture of the rearranged products 1-phenylbicyclo[2.2.2]octane (**18c**) and -bicyclo[3.2.1]octane (**19c**) (Table VI). Finally, irradia-

Table X. Irradiation of 1-Iodomethylnorbornane (**15a**) in Methanol-*O-d*[a]

λ	Time, h	Yield, %[b]	
		18a	19a
254 nm	8	43 D_0 100	57 D_0 100
Broad spectrum[c]	6	36 D_1 3 D_0 97	64 D_1 3 D_0 97

[a] Irradiations were conducted as described in the Experimental Section using 5-ml solutions containing 100 mg of iodide **15a**. [b] Relative yields as determined by gas chromatographic analysis. Isotopic compositions were determined by mass spectral analysis. [c] 450-W medium pressure mercury lamp.

tion of 1-iodooctane (**22a**) in benzene gave a mixture of the octenes **26** and **27**, the 1-phenyl derivative **28d**, and *n*-octane (Table VII). Attempts to sensitize 1-bromonorbornane (**1b**) in ether solution using acetophenone and Pyrex optics gave no reaction; similar attempts to sensitize the iodide **1a** were inconclusive because of slow photoconversion of **1a** under similar conditions in the absence of sensitizer.

Discussion

Ionic vs. Radical Photobehavior. From the above results it is seen that iodides **1a**, **10a**, **13a**, and **15a** afford principal photoproducts which are clearly derived from nucleophilic trapping of a cationic intermediate. These products are usually accompanied by the corresponding free radical (reduction) product, but in much lower yields. From these results, as well as those of our previous study on the photochemical behavior of 2-iodonorbornanes,[8a] it is clear that cationic, as well as free radical, intermediates play a major role in the solution-phase photochemistry of alkyl halides, contrary to the earlier belief that only radical intermediates are principally involved.[4]

We have previously proposed that radical and carbocationic photoproducts from alkyl halides are coupled, as shown in Scheme I, through the common intermediacy of the radical pair (II), which undergoes electron transfer to afford an ion pair (III) in competition with dissociation to free radicals and, ultimately, radical products.[8a] The present results strongly support this mechanism. Thus, for example, irradiation of 1-iodonorbornane (**1a**) in methanol saturated with oxygen instead of nitrogen resulted in complete quenching of the formation of the reduction product, norbornane (**8**), and substantial quenching of the formation of the ionic product **3a.** This is readily explained in terms of trapping of norbornyl radical by oxygen to form the hydroperoxide **9**, in competition with the electron transfer process. Reductive workup then affords the observed major photoproduct, 1-norbornanol (**6**). Both the low quantum yield for disappearance of **1a** and its increase in the presence of oxygen suggest that there is substantial recombination within the radical pair **5** (and probably also the ion pair **2**) to regenerate the starting iodide **1a.**

The substantially attenuated ionic behavior of bromides as compared with their iodo analogues is at first surprising in that it might be expected that the more electronegative bromine would undergo electron transfer more readily than iodine. There are, however, several possible offsetting effects. Bromine atoms may well abstract hydrogen atoms from the solvent cage in competition with the electron transfer process, whereas the much less reactive iodine atoms are incapable of this. The greater polarizability of iodine might facilitate electron transfer. Finally, the larger iodide ion affords a lower charge density. The origin of the solvent effect, in which the use of ethylene glycol affords increased yields of ionic products from both bromides and iodides, is thought to be due at least in part to an extended lifetime of the radical pair in the more viscous medium, which permits electron transfer to compete more favorably with diffusion of the radical components from the caged pair.

Cations generated at the 1-norbornyl and 1- and 2-adamantyl positions by photolysis of the corresponding halides were readily trapped in nucleophilic media to afford various substitution products. Elimination is inhibited in these systems because of the inherent strain of the resulting bridgehead olefin. On the other hand, the cation generated by photolysis of 1-iodooctane (**22a**) underwent almost exclusive elimination and afforded not only the expected 1-octene, but also substantial amounts of the rearranged 2- and 3-octenes.[14] Only very small amounts of substitution products were obtained and these included both the 1- and 2-isomers. The preference for elimination and the tendency to undergo prior positional migration are characteristics of "free" cations generated by high-energy processes with little or no solvent participation.[16] By contrast, the exclusive formation of the 1-octyl ether **28a** on treatment of 1-iodooctane (**22a**) with methanolic silver perchlorate solution is indicative of substantial involvement by solvent in this ground-state process. As expected, the 1-octyl radical underwent predominant, if not exclusive, hydrogen atom abstraction, in preference to either disproportionation or coupling.[17]

Additional evidence for the intermediacy of "free" cations is gained from the observed rearrangement of the 1-norbornylmethyl cation to a 1:1.3–1.4 mixture of bicyclo[2.2.2]- and bicyclo[3.2.1]octyl derivatives **18** and **19**, respectively, as displayed in Scheme V. This is in contrast to the ground-state silver ion assisted methanolysis of 1-iodomethylnorbornane (**15a**), which afforded predominantly the bicyclo[2.2.2]octyl derivative **18a** (61%), accompanied by the unrearranged derivative **21** (12%) and only a small amount (6%) of the bicyclo[3.2.1]octyl derivative **19a.**[18] Preferential isomerization of the 1-norbornylmethyl cation to a bicyclo[2.2.2]octyl rather than bicyclo[3.2.1]octyl derivative has been observed in other ground-state reactions.[19] The contrasting photochemical behavior to afford the 1-bicyclo[2.2.2]octyl and 1-bicyclo-[3.2.1]octyl cations in almost a statistical ratio most likely results from the free, non-solvent-associated nature of the initially formed 1-norbornylmethyl cation. It is interesting to note that 1-iodomethylnorbornane (**15a**) afforded substantially less reduced product than 1-iodooctane (**22a**) even though both systems are primary. Electron transfer may be facilitated in the case of **15a** because of σ-delocalized stabilization that is available to the 1-norbornylmethyl cation but not the radical.

Deuterium Incorporation. The formation of ether **3a** on irradiation of 1-iodonorbornane (**1a**) in methanol-*O-d* with no detectable incorporation of deuterium rules out the intervention of such conceivable intermediates as 1-norbornene or [2.2.1]propellane, which could arise via a 1,2- or 1,4-elimination of hydrogen iodide, respectively, and suggests that reaction involves simple formation and trapping of the 1-norbornyl cation. Similarly, the formation of ethers **18a** and **19a** on irradiation of 1-iodomethylnorbornane (**15a**) in methanol-*O-d* with little or no incorporation of deuterium rules out several conceivable mechanisms involving a carbene intermediate. Again, simple formation of the 1-norbornylmethyl cation followed by ring expansion and nucleophilic trapping is suggested.

Although hydrogen atom abstraction from the solvent by the corresponding radical intermediate is most likely the predominant mode for formation of the reduction products, the incorporation of small but significant amounts of deuterium in the reduction product norbornane (**8**) indicates that it is not always the exclusive pathway. As outlined in Scheme II, a possible origin of deuterium in norbornane (**8**) is protonation of the 1-norbornyl carbanion (**7**), which arises via nucleophilic attack by methanol on bromine or iodine in the n, σ^* excited state (**4**). The n $\rightarrow \sigma^*$ transition results in a change of polarization as indicated.[9d,f] Although tertiary, the 1-norbornyl carbanion (**7**) is stabilized by a strain-induced increase in s character in the exocyclic carbon orbital.[20] Alternatively, the deuterium incorporation may arise via abstraction from deuterium iodide, formed from exchange of hydrogen iodide with the solvent.

Triethylamine. In the presence of 1 mol equiv of triethylamine the reduction products were obtained predominantly, if not exclusively. Moreover, in methanol-*O-d* norbornane (**8**) was obtained with no deuterium incorporation. Reaction in this case probably involves photochemical decomposition of a weakly bound amine-halide pair.[21]

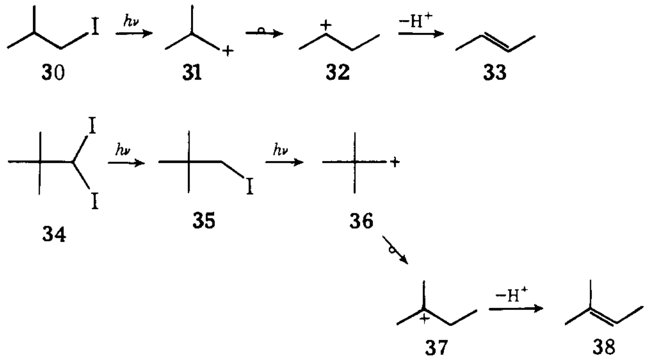
$$\mathrm{RX \cdot NEt_3} \xrightarrow{h\nu} \mathrm{RX\cdot^- \; {}^{+}\cdot NEt_3} \rightarrow \mathrm{R\cdot + X^- \; {}^{+}NEt_3}$$

Sensitization. Irradiation of alkyl iodides in benzene solution at 254 nm probably involves photosensitization, since benzene absorbs strongly at this wavelength. However, since iodides also absorb at 254 nm, it is not clear whether transfer occurs from singlet or triplet benzene. It is also not clear whether trapping involves a radical or cationic intermediate. Irradiation of 1-iodonorbornane (**1a**) in benzene afforded the 1-phenyl derivative **3** (R = C_6H_5), which could arise via attack of benzene on either the 1-norbornyl radical or cation. However, irradiation of **1a** in toluene afforded a mixture of *o*-, *m*- and *p*-tolyl derivatives **3** (R = $CH_3C_6H_4$), in which the ortho isomer predominated. The observed ratios (51:28:21, ortho-meta-para) more closely resemble those obtained on reaction of toluene with methyl radical (59:26:15)[22] than the ratios obtained from reaction with 1-apocamphyl cation (23:46:31).[23] Thus it appears that trapping involves at least principally the 1-norbornyl radical. On the other hand, irradiation of 1-iodomethylnorbornane (**15a**) in benzene afforded the rearranged derivatives 1-phenylbicyclo[2.2.2]octane (**18c**) and -bicyclo[3.2.1]octane (**19c**). Since such skeletal rearrangements are more characteristic of cationic than radical intermediates, it appears in this case that electron transfer to ion pair **17**, followed or accompanied by ring expansion to the bicyclooctyl skeletons **18** and **19**, precedes trapping. As noted above, electron transfer may be facilitated in this case because of the stability of the resulting carbocation.

Concluding Remarks

It is clear from the present results that irradiation of alkyl bromides and, particularly, iodides in solution is a convenient and powerful means for the generation of carbocationic intermediates. Surprisingly, this phenomenon was not previously recognized despite extensive prior study of the photochemistry of alkyl halides.[4] In retrospect, recognition of the involvement of cationic intermediates in the photochemistry of alkyl iodides provides obvious answers to some of the apparent anomalies in the earlier literature, which were formerly inexplicable because only radical intermediates were considered. Thus, for example, isobutyl iodide (**30**) was found to afford a mixture of isobutane and rearranged 2-butene (**33**) (Scheme VII); only small amounts of unrearranged olefin were formed.[6a] The formation of 2-butene (**33**) can now be explained via rearrangement of the isobutyl cation (**31**). Similarly, irradiation of diiodide **34** was found to afford substantial amounts of 2-methyl-2-butene (**38**);[24] this can now be explained via initial formation of neopentyl iodide (**35**), followed by secondary photolysis of **35** to afford the neopentyl cation (**36**), which undergoes rearrangement and proton loss to afford **38**.

Scheme VII



Experimental Section

General. Infrared spectra were obtained either neat or in carbon tetrachloride or chloroform solution using a Perkin-Elmer 421 grating spectrophotometer and ultraviolet spectra were obtained in absolute ethanol solution using a Cary 14 or 17 spectrophotometer. Gas chromatographic analyses, except for quantum yields, were performed on a Varian Aerograph 90-P or a Hewlett-Packard 5750 instrument using 10 ft × 0.25 in. stainless steel columns containing either 20% SF-96 or 20% Carbowax 20M on 60-80 mesh Chromosorb W. Melting points were determined using a Thomas-Hoover capillary apparatus and are uncorrected and uncalibrated. Proton magnetic resonance spectra were determined in either carbon tetrachloride or chloroform-*d* solutions with a Jeolco C-60HL spectrometer or a Varian XL-100 spectrometer, using 0.3% tetramethylsilane as an internal standard; data are reported in the following manner: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br = broadened); integration; coupling constant (given in Hz); and assignment when possible. Mass spectra were obtained using either a Hitachi Perkin-Elmer RMU-6E or an AEI MS-902 spectrometer; *m/e* values reported include the parent ion peak, if detectable, and other significantly large peaks appearing above *m/e* 55.

Irradiations were conducted either (A) at 254 nm using a quartz vessel with an attached condenser and nitrogen inlet tube suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 (254 nm) lamps or (B) with the broad mercury spectrum using either a Hanovia 450-W medium arc immersion lamp placed into an Ace double-walled, water-cooled, quartz immersion well which was fitted in a 100-ml Pyrex reaction vessel equipped with a magnetic stirring bar, condenser, and nitrogen inlet tube or an air-cooled quartz tube with an attached condenser and nitrogen inlet tube suspended approximately 6 cm in front of a Hanovia 450-W medium arc reflector lamp. The quartz vessels were either tubes or flasks individually made of 2-mm wall thickness General Electric type 204 clear fused quartz. The tubes (18-27 cm length × 9 mm i.d. × 11 mm o.d.) were sealed at the bottom and were fused at the top to a ₸ 14/35 Vycor joint for placement of a condenser. The flasks were of round-bottomed shape with either a 10-, 25-, or 50-ml volume size and also fused to a ₸ 14/35 Vycor joint.

In all cases, except the quartz tube irradiations, stirring of the reaction mixture was effected by the use of Teflon-covered magnetic stirring bars. Except where otherwise indicated, all irradiations were carried out under a nitrogen atmosphere that was achieved either by use of five successive nitrogen purge cycles with a nitrogen bubbler apparatus or by bubbling nitrogen gas through the solution for 10 min prior to the irradiation. Where indicated, finely divided mossy zinc was used as a scavenger for liberated iodine and hydrogen iodide. Except where indicated, control studies showed no reaction in the absence of light before or after irradiation, even in the presence of added iodine, zinc iodide, hydrogen iodide, or triethylamine.

All solvents used in the irradiations were dried and/or purified by the following procedures: methanol, stored over 3A molecular sieves; *tert*-butyl alcohol, distilled from calcium hydride; diethyl ether, diglyme, and tetrahydrofuran, distilled from lithium aluminum hydride; acetonitrile, spectroquality used directly from the bottle; ethylene glycol, distilled from barium oxide and then stored over 3A molecular sieves; acetone, Fisher spectroanalyzed distilled from potassium permanganate and then stored over 3A molecular sieves; benzene, Fisher spectroanalyzed recrystallized four times in an ice-salt bath; pentane, passed through alumina and then fractionally distilled.

After the irradiation had been completed, the usually yellow solution was poured into 50 ml of water and extracted with four 5-ml portions of pentane or ether. The combined organic layers were washed with a 5-ml portion of 10% aqueous sodium thiosulfate solution and a 5-ml portion of saturated sodium bicarbonate solution. At this time a white, gelatinous precipitate of zinc carbonate would appear if zinc iodide was present in the solution. The organic phase was washed with a 5-ml portion of water and then a 5-ml portion of saturated sodium chloride solution, dried over anhydrous granular sodium sulfate, and subsequently filtered. The solvent was removed by distillation through a 1-ft Vigreux column.

Control experiments were generally run on solutions of 50–100 mg of halide contained in covered Pyrex vessels maintained at the same temperature as the irradiation mixtures.

1-Halonorbornanes (1). A. Preparation. 1-Iodonorbornane (**1a**) was prepared as described previously.[25] 1-Bromonorbornane (**1b**)[26] was prepared by a modification of the Cristol–Firth Hunsdiecker procedure[27] as recently reported.[28]

B. Photoproducts. 1-Methoxy- (**3a**), 1-ethoxy- (**3b**),[11] 1-chloro- (**3d**),[29] 1-phenyl- (**3**, R = C_6H_5),[30] and 1-*o*-tolylnorbornane (**3**, R = *o*-$CH_3C_6H_4$), *N*-(1-norbornyl)acetamide (**3e**), and 1-norbornanol (**6**)[31] were obtained as previously described.[28]

1-(3-Butenoxy)norbornane (**3c**) was isolated as a colorless liquid: ν_{max} (CCl_4) 3079, 2957, 2921, 2873, 1640, 1453, 1320, 1216, 1225, 1172, 1142, 1103, 988, and 917 cm^{-1}; ^1H NMR (CCl_4) τ 4.10 (t × d × d, 1, J = 6.6, 9.8, and 17.3 Hz, -CH=), 4.94 (m, 2, =CH_2), 6.54 (t, 2, J = 7.3 Hz, CH_2O), 7.65 (t, 2, J = 7.3 Hz, CH_2), and 7.91 (br s, 1, CH-4); *m/e* 166.1356 (calcd for $C_{11}H_{18}O$, 166.1358), 137 (56), 84 (43), 83 (70), and 55 (100).

1-*tert*-Butoxynorbornane (**3g**) was obtained as a colorless liquid: ν_{max} (CCl_4) 2959, 2823, 1452, 1386, 1360, 1315, 1261, 1221, 1189, 1162, 1134, 1101, and 889 cm^{-1}; ^1H NMR (CCl_4) τ 8.07 (br s, 1, CH-4) and 8.76 (s, 9, $(CH_3)_3C$); *m/e* 168.1512 (calcd for $C_{11}H_{20}O$, 168.1514), 111 (96), 96 (43), 94 (57), 82 (100), and 70 (96).

1-(2-Hydroxyethoxy)norbornane (**3**, R = OCH_2CH_2OH) was obtained as a clear oil: ν_{max} (CCl_4) 3431, 2957, 2925, 2872, 1452, 1319, 1262, 1179, 1141, 1071, and 891 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.31 (m, 4, CH_2CH_2), 7.5 (s, 1, OH) and 7.87 (br s, 1, CH-4); *m/e* 156.1148 (calcd for $C_9H_{16}O_2$, 156.1150), 127 (39), 113 (34), 95 (25), and 83 (100).

1-*m*- and -*p*-Tolylnorbornane (**3**, R = *m*- and *p*-$CH_3C_6H_4$) were isolated as a mixture: ν_{max} (neat) 3055, 3025, 2950, 2922, 2873, 1603, 1508, 1486, 1450, 1329, 1300, 802, 773, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) τ 2.73 (m, 5, aromatic H) and 7.64 (s, 3, Ar-CH_3); *m/e* 186.1405 (calcd for $C_{14}H_{18}$, 186.1408), 186 (45), and 147 (100).

Norbornane (**8**) was obtained as a colorless solid which was identical in every respect with a commercial specimen.

1- and 2- Haloadamantanes (10 and 13). A. Preparation. 1-Iodoadamantane (**10a**) was prepared as described previously.[32] Both 1- (**10b**) and 2-bromoadamantane (**13b**) were obtained commercially.

2-Iodoamantane (**13a**) was prepared following a modification of the procedure suggested by the work of Lenoir with some dihaloadamantanes.[33] Into a 100-ml, round-bottomed flask equipped with a magnetic stirring bar, condenser, and a nitrogen inlet tube were placed 1.12 g (0.521 mmol) of 2-bromoadamantane (**13b**), 12.3 g (74.1 mmol) of anhydrous potassium iodide, and 25 ml of hexamethylphosphoramide. The resulting clear mixture was purged with nitrogen and allowed to heat to 150 °C for 72 h while stirring, during which time the reaction mixture became colored. The brown mixture was then allowed to cool and poured into 400 ml of water and extracted with four 50-ml portions of ether. The combined yellow ether layers were washed once with successive 10-ml portions of 10% sodium thiosulfate solution, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. After filtration, the ether was removed by distillation through a 1-ft Vigreux column, yielding a yellow oil which was shown by gas chromatographic analysis to be 90% pure. The oil slowly solidified at room temperature over a period of 2 weeks to afford 1.32 g of white crystals, which, after two recrystallizations from hot methanol, yielded 735 mg (0.280 mmol, 54% yield) of **13a** as colorless crystals: mp 47.5–48.5 °C; λ_{max} (EtOH) 257 (ϵ 754), (pentane) 258 nm (ϵ 767); ν_{max} (CCl_4) 2961, 2856, 1463, 1442, 1346, 1268, 1210, 1151, 1092, 951, 890, and 706 cm^{-1}; ^1H NMR ($CDCl_3$) τ 4.94 (br s, 1, CH-2); lit. mp 46–48 °C.[34]

B. Photoproducts. Adamantane (**11**) was obtained as a colorless solid which was identical in every respect with a commercial specimen. 1-Methoxyadamantane (**12a**) was obtained as described previously.[28] 1-Ethoxy- (**12b**)[35] and 2-methoxyadamantane (**14a**)[34] had spectral data identical with those previously reported.

1-(2-Hydroxyethoxy)adamantane (**12c**) was obtained as a colorless, waxy solid: mp 37–39 °C; ν_{max} (CCl_4) 3595, 3479, 2914, 2855, 1447, 1394, 1366, 1350, 1300, 1201, 1113, 1086, 1065, 1042, 971, 941, 886, and 843 cm^{-1}; ^1H NMR (CCl_4) τ 6.42 (br s, 5, OCH_2CH_2OH) and 7.77 (br s, 3, CH-3,5,7); lit.[36] ^1H NMR (CCl_4) τ 7.42, 7.85, 8.26, and 8.33.

2-Ethoxyadamantane (**14b**) was identical with a specimen synthesized independently. Sodium hydride, 270 mg (11.3 mmol), was added under a nitrogen atmosphere to a solution of 1.03 g (6.85 mmol) of 2-adamantanol dissolved in 50 ml of anhydrous glyme (distilled from lithium aluminum hydride), and contained in a 100-ml flask equipped with a magnetic stirring bar, a condenser, and a nitrogen inlet tube. After all gas evolution had ceased, 4.62 g (29.6 mmol) of ethyl iodide was slowly added over a period of 1 h and the resulting solution allowed to stir at 60 °C overnight. The clear, slightly yellow reaction solution was then poured into 400 ml of water and extracted thoroughly with four 50-ml portions of ether. The combined ether layers were washed successively with 25-ml portions of water and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. After filtration, the ether was removed by distillation through a 1-ft Vigreux column to yield a concentrated reaction mixture, which on gas chromatographic analysis showed the presence of one compound. The ether was then isolated as a clear liquid by preparative gas chromatography: ν_{max} (CCl_4) 2975, 2904, 2854, 1449, 1375, 1360, 1103, 1069, 1010, 959, 939, 882, and 722 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.45 (q, 2, J = 7.0 Hz, -OCH_2CH_3), 6.55 (br m, 1, CH-2), and 8.76 (t, 3, J = 7.0 Hz, -OCH_2CH_3); lit.,[37] no spectral data given.

2-(2-Hydroxyethoxy)adamantane (**14c**) was obtained as a colorless, waxy solid: mp 39–41 °C; ν_{max} (CCl_4) 3596, 3473, 2905, 2856, 1447, 1360, 1333, 1201, 1105, 1052, 1010, and 987 cm^{-1}; ^1H NMR (CCl_4) τ 7.4 (m, 5, OCH_2CH_2OH); *m/e* 196.1465 (calcd for $C_{12}H_{20}O_2$, 196.1463), 196 (10), 135 (100), 134 (41), 93 (21), 79 (25), and 67 (21).

1-Halomethylnorbornanes (15). A. Preparation. 1-Iodomethylnorbornane (**15a**) was prepared according to the general procedure of Tipson et al.[38] 1-Norbornylmethyl tosylate,[29] 5.80 g (21.6 mmol), was added to a solution of 8.84 g (58.8 mmol) of sodium iodide in 100 ml of anhydrous acetone contained in a dry 200-ml round-bottomed flask equipped with a magnetic stirring bar, condenser, and a nitrogen inlet tube. The flask was purged with nitrogen and the mixture allowed to reflux with stirring under nitrogen for 10 h, during which time the solution turned yellow and a silvery white solid appeared. After the solid had been removed by filtration and the filtrate added to 250 ml of water, the solution was extracted with four 40-ml portions of pentane. The combined pentane layers were washed successively with 15-ml portions of water and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. After filtration, the pentane was removed by distillation to yield approximately 45 g of a pale yellow liquid which, upon fractional distillation under reduced pressure, 71 °C (6 mm), afforded 3.99 g (16.9 mmol, 79% yield) of the iodide **15a** as a colorless liquid: λ_{max} (EtOH) 255 nm (ϵ 663); ν_{max} (neat) 2950, 2916, 2870, 1445, 1326, 1300, 1247, 1230, 1202, 1173, 1149, and 919 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.48 (s, 2, CH_2-8) and 7.62 (br s, 1, CH-4); *m/e* 236.0061 (calcd for $C_8H_{13}I$, 236.0064), 110 (14), 109 (100), 71 (18), and 67 (35).

1-Bromomethylnorbornane (**15b**) was prepared employing the method of Wiberg and Lowry.[39] Short-path distillation at 67–68 °C (2.5 mm) with a Kugelrohr apparatus afforded the bromide as a colorless liquid: ν_{max} (neat) 2950, 2918, 2895, 2871, 1449, 1429, 1330, 1300, 1254, 1236, 1218, 1190, 1028, 951, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.44 (s, 2, CH_2-8), and 7.72 (br s, 1, CH-4); lit.[39] bp 89 °C (20 mm).

B. Photoproducts. 1-Methoxybicyclo[2.2.2]octane (**18a**) was isolated as a colorless liquid: ν_{max} (CCl_4) 2948, 2869, 2830, 1452, 1343, 1320, 1253, 1182, 1111, 1099, 1026, 981, 907, 889, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.84 (s, 3, OCH_3) and 8.38 (m, 13); lit.[40] ν_{max} 2822, 1116, and 1106 cm^{-1}.

1-Ethoxybicyclo[2.2.2]octane (**18b**) was isolated as a clear liquid: ν_{max} (CCl_4) 2977, 2949, 2922, 2870, 1452, 1390, 1346, 1321, 1255, 1109, 1043, 983, 942, 910, 864, and 724 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 6.62 q, 2, J = 7.1 Hz, OCH_2CH_3), 8.38 (br m, 13), and 8.87 (t, 3, J = 7 Hz, OCH_2CH_3); *m/e* 154.1363 (calcd for $C_{10}H_{18}O$, 154.1358), 154 (25), 125 (100), 98 (64), 70 (61), and 69

(95).

1-Phenylbicyclo[2.2.2]octane (**18c**) was isolated as a colorless, waxy solid: mp 80-81 °C (sealed tube); ν_{max} (CCl_4) 3089, 3062, 3049, 3038, 3042, 3020, 2868, 1941, 1860, 1800, 1600, 1454, 1446, 1351, 1333, 1260, 1077, 1036, 1000, 990, 907, 894, 745, 725, and 697 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 2.73 (m, 5, aromatic H) and 8.27 m, 13) with shoulder at 8.49; lit.[41] ν_{max} 2910, 2825, 1590, 1490, 755, and 695 cm^{-1}; ^1H NMR 2.65-2.97 (m, 5) and 8.28-8.47 (br m, 13).

1-Iodobicyclo[2.2.2]octane (**18d**) as isolated was identical with material prepared independently by the addition of anhydrous hydriodic acid to 1-norbornylmethanol as described below: mp 25.8-27.4 °C (sealed capillary); λ_{max} (EtOH) 261 nm (ϵ 905); ν_{max} (CCl_4) 2949, 2924, 2871, 1456, 1389, 1311, 1260, 968, 895, 823, and 728 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 7.52 (m, 6) and 8.34 (m, 6); lit.[40] mp 27.5-28.5 °C.

1-Methoxybicyclo[3.2.1]octane (**19a**) was isolated as a clear, colorless liquid: ν_{max} (CCl_4) 2941, 2862, 2857, 2838, 1476, 1450, 1339, 1312, 1301, 1260, 1195, 1141, 1102, 1058, 1041, 1010, 981, 960, 924, 870, and 721 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 6.73 (s, 3, OCH_3) and 7.77 (br s, 1, bridgehead H); *m/e* 140.1205 (calcd for $C_9H_{16}O$, 140. 1201), 140 (9), 111 (40), 97 (100), and 69 (35).

1-Ethoxybicyclo[3.2.1]octane (**19b**) was isolated as a colorless liquid: ν_{max} (CCl_4) 2978, 2940, 2871, 1477, 1452, 1390, 1341, 1315, 1301, 1259, 1200, 1143, 1109, 1061, 1015, 973, 941, 913, and 724 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 6.54 (q, 2, J = 7.0 Hz, $-OCH_2CH_3$), 7.79 (br s, 1, bridgehead H), and 8.83 (t, 3, J = 7.0 Hz, OCH_2CH_3); *m/e* 154.1363 (calcd for $C_{10}H_{18}O$, 154.1358), 125 (31), 111 (100), 97 (35), and 83 (47).

1-Phenylbicyclo[3.2.1]octane (**19c**) was isolated as a colorless oil: ν_{max} (CCl_4) 3087, 3062, 3028, 2940, 2871, 2857, 1600, 1491, 1451, 1442, 1346, 1073, 1026, 1012, 741, 720, and 695 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 2.74 (m, 5, aromatic H) and 7.68 (br s, 1, bridgehead H); *m/e* 186.1410 (calcd for $C_{14}H_{18}$, 186.1408), 186 (29), 157 (22), 144 (18), 143 (100), 128 (24), 105 (21), and 91 (32).

1-Iodobicyclo[3.2.1]octane (**19d**) was isolated as a colorless liquid: ν_{max} (CCl_4) 2946, 2873, 1454, 1340, 1316, 1260, 1240, 1187, 1057, 1001, 980, 950, 888, and 825 cm^{-1}; ^1H NMR [($CDCl_3$) 100 MHz-FT] τ 7.75 (complex multiplet); *m/e* 236.0069 (calcd for $C_8H_{13}I$, 236.0064), 119 (40), and 67 (100). Similar material was also isolated from the treatment of 1-norbornylmethanol with hydriodic acid as described below.

1-Methylnorbornane (**20**) was isolated as previously described.[28]

C. **Treatment of 1-Norbornylmethyl with Hydriodic Acid.** To a mixture of 1.9 g of 85% phosphoric acid and 0.55 g of phosphoric anhydride contained in a 50-ml round-bottomed flask equipped with a magnetic stirring bar, condenser, and nitrogen inlet tube were added 3.1 g of anhydrous potassium iodide and 455 mg of 1-norbornylmethanol. The resulting mixture was heated to 100 °C for 5 h and maintained at room temperature an additional 24 h with stirring under an atmosphere of nitrogen. Water (20 ml) was added followed by 10 ml of ether and the resulting mixture was stirred. The ether layer was separated and the aqueous phase was extracted with four additional 5-ml portions of ether. The combined ether fractions were washed with two 5-ml portions of saturated sodium bicarbonate solution and a 5-ml portion of each of 10% sodium thiosulfate solution, water, and saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. Removal of ether by distillation afforded a yellow liquid which was shown by gas chromatographic analysis to consist of iodides **15a**, **18a**, and **19a** in yields of 40, 49, and 11%, respectively.

D. **Methanolysis of 1-Iodomethylnorbornane** (**15a**). To a solution of 796 mg of iodide **15a** in 40 ml of methanol was added 699 mg of silver perchlorate, and the resulting mixture was stirred for 2 h at room temperature. An immediate yellow precipitate was formed, which was removed by filtration. The filtrate was diluted with 200 ml of water and extracted with four 40-ml portions of ether. The combined ether fractions were dried over 10 ml of saturated sodium chloride solution and then anhydrous sodium sulfate and concentrated by distillation to afford a colorless oil, which was shown by gas chromatographic analysis to consist of iodide **15a** and ethers **18a**, **19a**, and **21** in yields of 20, 61, 6, and 12%, respectively.

Isolation of 1-methoxymethylnorbornane (**21**) by preparative gas chromatography afforded a colorless liquid: ν_{max} (CCl_4) 2951, 2931, 2896, 2872, 2827, 1448, 1387, 1333, 1187, 1101, and 951 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.56 (s, 2, $-CH_2OCH_3$), 6.64 (s, 3, OCH_3), and 7.81 (br 2, 1, bridgehead H); *m/e* 140.1202 (calcd for $C_9H_{16}O$, 140.1201), 140 (48), 121 (55), 118 (100), 93 (54), 80 (55), 79 (83), and 71 (55).

Irradiation of 1-Halooctanes (**22**). Commercial specimens of 1-iodo- (**22a**) and 1-bromooctane (**22b**) were employed. *n*-Octane (**24**), 1-octene (**26**), 1-octanol (**28c**), and 1-phenyloctane (**28d**) were characterized by direct comparison with commercial specimens.

The other four octenes (*cis*- and *trans*-2-octene, and *cis*- and *trans*-3-octene), collectively known as **29**, were obtained as an inseparable mixture on preparative scale gas chromatography. They were individually identified by comparison of their gas chromatographic retention times with those of commercial samples on a 20 ft × ¼ in. column packed with 20% β,β-oxydipropinitrile on Chromosorb P, using analytical scale injections. Because no separation was achieved on preparative scale levels, ^1H NMR analysis was employed to determine the relative amounts of these olefins that were present.

1-Methoxyoctane (**28a**) was isolated as a colorless, clear, sweet smelling liquid: ν_{max} (CCl_4) 2960, 2930, 2861, 2830, 2812, 1459, 1384, 1192, 1116, 948, and 719 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.55 (t, 2, J = 6.7 Hz, CH_2-1), 6.57 (s, 3, OCH_3), 8.65 (m, 12), and 9.09 (t, 3, J = 4.2 Hz, CH_3-8); lit.,[42] no spectral data given.

1-(2-Hydroxyethoxy)octane (**28b**) was isolated as a colorless liquid: ν_{max} (CCl_4) 3605, 3565, 3300, 2958, 2930, 2860, 1455, 1390, 1377, 1350, 1239, 1210, 1119, 1054, and 885 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.36 (m, 6, $-CH_2OCH_2CH_2OH$), 7.91 (s, 1, OH), 8.66 (m, 12), and 9.09 (t, 3, J = 4.2 Hz, CH_3-8); lit.,[43] no spectral data given.

2-Methoxyoctane (**29a**) was isolated as a colorless liquid and was identified by its relative gas chromatographic retention time and spectral characteristics to that of the similar methyl ether **30b**: ν_{max} (CCl_4) 2963, 2930, 2862, 1461, 1376, 1092, 909, and 720 cm^{-1}; ^1H NMR (CCl_4) τ 6.53 (br s, 4, CH-2, and OCH_3), 8.69 (m, 10), 8.86 (d, 3, J = 6.5 Hz, CH_3-1), and 9.07 (m, 3, CH_3-8); lit.,[42] no spectral data given.

2-(2-Hydroxyethoxy)octane (**31c**) was isolated as a colorless liquid: ν_{max} (CCl_4) 3598, 3545, 3300, 2960, 2930, 2862, 1457, 1371, 1332, 1236, 1206, 1097, 1049, 887, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.38 (m, 5, $-CHOCH_2CH_2OH$), 7.93 (s, 1, OH), 8.66 (m, 10), 8.84 (d, 3, J = 6.4 Hz, CH_3-2), and 9.08 (m, 3, CH_3-8); lit.,[43] no spectral data given.

2-Iodooctane (**29c**) as isolated was identical with an authentic specimen synthesized independently by the general procedure of Stone and Schecter[44] to afford a pale orange liquid: bp 56-57 °C (6.0 mm); λ_{max} (EtOH) 260 nm (ϵ 619); ν_{max} (neat) 2901, 2931, 2860, 1450, 1372, 1200, 1161, 1129, 783, and 721 cm^{-1}; ^1H NMR ($CDCl_3$) τ 5.78 (m, 1, CH-2), 8.05 (d, 3, J = 6.9 Hz, CH_3-1), 8.71 (m, 10), and 9.08 (t, 3, J = 7.6 Hz, CH_3-8).

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Strained Ring Systems. 16.[1a] Substituent Effects on the pK_a Values of *cis*- and *trans*-1,2-Dimethyl-2-X-cyclopropane-1-carboxylic Acids and Related Bicyclo[*n*.1.0]alkane-1-carboxylic Acids

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Abstract: The syntheses of certain 3-X-bicyclo[1.1.0]butane-1-carboxylic acids ([1.1.0] **1**; X = $CONH_2$, CO_2CH_3, CO_2H), *cis*- (cis **4**; X = H, CO_2CH_3, Br, CO_2H) and *trans*-1,2-dimethyl-2-X-cyclopropane-1-carboxylic acids (trans **5**; X = H, $CONH_2$, CO_2CH_3, Br, CN, CO_2H), are reported. The thermodynamic pK_a values in water at 25 °C were determined for these compounds as well as the related derivatives of 5-X-bicyclo[3.1.0]hexane-1-carboxylic acid ([3.1.0] **3**; X = H, $CONH_2$, CO_2CH_3, Br, CN, CO_2H) and 4-X-bicyclo[2.1.0]pentane-1-carboxylic acid ([2.1.0] **2**; X = H, $CONH_2$, CO_2CH_3, CN, CO_2H) previously syntheized, as were the pK_2 values for the dicarboxylic acids. Plots of pK_a values vs. σ_I substituent constants for these five series of acids, and of the substituent effects in the cis **4**, [3.1.0] **3**, [2.1.0] **2**, and [1.1.0] **1** series relative to that same substituent's effect in the trans **5** series where intramolecular hydrogen bonding is not possible are developed and discussed. In general, intramolecular hydrogen bonding in these four series of acids, **1–4**, was at a maximum in the [2.1.0] **2** series and minimal in the [1.1.0] **1** series. This is unusual since intramolecular hydrogen bonding was predicted to be the greatest in the [1.1.0] **1** series on the basis of the distance separating X and CO_2H at the bridgeheads. This anomaly was resolved by considering a strong ring C_1–C_3 bond interaction with CO_2H carbonyl carbon stabilizing the *perpendicular* conformer (**15**). This approach was supported by INDO MO calculations on bicyclo[1.1.0]butane-1-carboxylic acid and its carboxylate anion where the *perpendicular* conformations were preferred in both structures by 5.2 and 3.1 kcal/mol, respectively. A related but attenuated effect was presented to explain the lower than predicted acidity of cyclopropanecarboxylic acid which was used to discuss the substituent effects in the trans **5** and cis **4** series.

In the area of structure–property relationships of aliphatic compounds, the change in the acidities of carboxylic acids with structural variations continues to be a frequently used probe. The effects of remote, nonconjugated substituent groups on the reaction center have been examined by both the inductive and field effect models.[2] The results of various recently reported studies with several polycyclic systems[2,3] lead to the conclusion that the field model, not the inductive model, accurately describes the mechanism by which these substituent effects are transmitted. Correlations of such substituent effects with the empirical parameter σ_I have been successful, although the precise meaning of these correlations has been controversial.

From the above brief discussion we can conclude that the