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56413-47-9; iodosylbenzene, 536-80-1.

Supplementary Material Available: A listing of observed and calculated structure factors for the title compound (23 pages). Ordering information is given on any current masthead page.

Photochemistry of Alkyl Halides. 8. Formation of a Bridgehead Alkene¹

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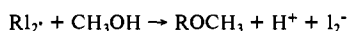
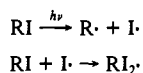
Abstract: Irradiation of the bridgehead iodides **4**, **7**, and **10** afforded principally the ionic products **6**, **9**, and **12** accompanied by small amounts of the reduction products **5**, **8**, and **11**. Studies in methanol-*d* indicated an absence of pathways leading to ethers **6**, **9**, and **12** involving bridgehead alkene or propellane intermediates. By contrast, the iodo ether **16** afforded not only the epimeric endo iodide **17**, the reduction product **19**, and the expected ionic products **23**, **24**, **27**, and **28** but also the rearranged iodide **25** and the ketals **26**. Deuterium labeling and trapping studies showed that these latter products arise via the intermediacy of the bridgehead alkene **20**. By contrast, the iodo lactone analogue **48** afforded only the reduction product **50** and the ionic products **51**, **52**, **54**, and **55**, with no detectable formation of products attributable to the intermediacy of the bridgehead alkene **61**. The factors involved in the formation of bridgehead alkene intermediate **20** are discussed.

Previous studies in these laboratories have shown that irradiation of alkyl iodides in solution is a powerful and convenient method for the generation of carbocations, via a process thought to involve initial light-induced homolytic cleavage of the carbon-iodine bond followed by electron transfer within the initially formed caged radical pair (Scheme I).² The powerfulness of the method was demonstrated by formation of the difficultly accessible 1-bicyclo[2.2.1]heptyl cation; irradiation of 1-iodobicyclo[2.2.1]heptane (**1**) in methanol or diethyl ether afforded principally the ether **3** (Y = OCH₃ or OC₂H₅), accompanied by a small amount of the radical product bicyclo[2.2.1]heptane (**2**).^{2a}

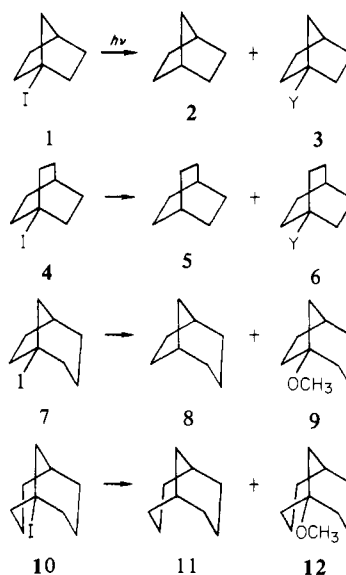
Similar studies involving other alkyl systems have revealed a marked propensity for carbocations generated photolytically from

(1) (a) Part 7: Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* 1981, 37, 3229-3236. (b) For a preliminary report of a portion of this work, see: Kropp, P. J.; Jones, T. H.; Poindexter, G. S. *J. Am. Chem. Soc.* 1973, 95, 5420-5421.

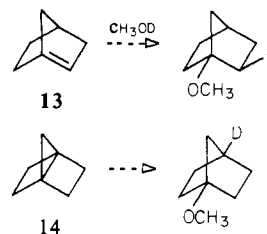
(2) (a) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* 1976, 98, 8135-8144. (b) A number of reports have appeared concerning the photosolvolysis of aralkyl halides: Zimmerman, H. E.; Sandel, V. R. *Ibid.* 1962, 85, 915-922. Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* 1973, 9, 345-347. Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* 1976, 2105-2108. Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* 1980, 87-90. Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* 1981, 103, 4625-4627. The last authors have recently presented evidence supporting the following mechanism for the photomethanolysis of 1-(iodomethyl)naphthalene:



Although such a mechanism may ultimately be found to be general for aralkyl iodides, it apparently does not apply, at least generally, to alkyl systems. Thus, the quantum yield for the formation of ether **3** (Y = OCH₃) from iodide **1** is substantially decreased by the presence of oxygen,^{2a} in agreement with the mechanism of Scheme I but not that outlined above. Moreover, preliminary studies in these laboratories have shown that the quantum yield for photo-conversion of 1-iodooctane is independent of the concentration of iodide **1**. Finally, iodide **1** is inert in a methanolic solution containing I₂, generated by irradiation of iodine at >280 nm.

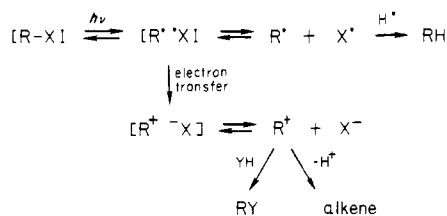


iodides to undergo 1,2 or 1,3 deprotonation in competition with nucleophilic trapping, even in alcoholic media.^{2a,3} However, similar deprotonation of the 1-bicyclo[2.2.1]heptyl cation would afford either the bridgehead alkene **13** or the propellane **14**, each

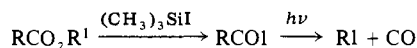


(3) Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* 1978, 207-210.

Scheme I



Scheme II

Table I. Irradiation of Bridgehead Iodides 4, 7, and 10^a

R1	solvent	yield, % ^b			
		R1	RH	RY	Y
4	CH ₃ OH	5	2	90	OCH ₃
	CH ₃ OD	8	2	88 ^c	OCH ₃
	(C ₂ H ₅) ₂ O	8	6	82	OC ₂ H ₅
7	CH ₃ OH	4	4	91	OCH ₃
	CH ₃ OD	2	5	93 ^c	OCH ₃
10	CH ₃ OH	<i>d</i>	15	81	OCH ₃
	CH ₃ OD	<i>d</i>	12	83 ^c	OCH ₃

^a Irradiations were conducted at 254 nm with 0.05 M solutions as described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. ^c Contained no deuterium detectable by mass spectrometric analysis. ^d Trace.

of which is highly strained. The possibility that either of these is formed initially but undergoes rapid reprotonation in protic media is precluded by the finding that irradiation of iodide 1 in methanol-*d* afforded ether 3 with no detectable incorporation of deuterium.^{2a} With the thought that larger ring systems would be more amenable to the formation of a bridgehead alkene or propellane derivative, the photobehavior of the bicyclic bridgehead iodides 4, 7, and 10 was investigated. As discussed below, none of these showed any detectable formation of unsaturated intermediates. However, quite different behavior was exhibited by the iodo ether 16.

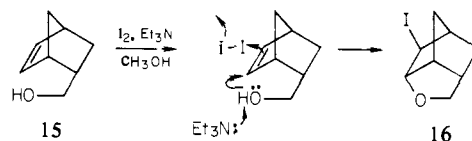
Results

Bridgehead Iodides 4, 7, and 10. 1-Iodobicyclo[2.2.2]octane (4) was prepared as described previously,⁴ whereas the analogues 7 and 10 were synthesized via a new procedure that should be generally applicable for the preparation of iodides (Scheme II). Treatment of the readily available bridgehead esters with iodotrimethylsilane afforded the corresponding acyl iodides,⁵ which underwent facile decarbonylation upon subsequent irradiation. The resulting iodides could be isolated in good yield if irradiation was terminated at this point. Alternatively, irradiation could be continued to afford photoproducts from the iodide.

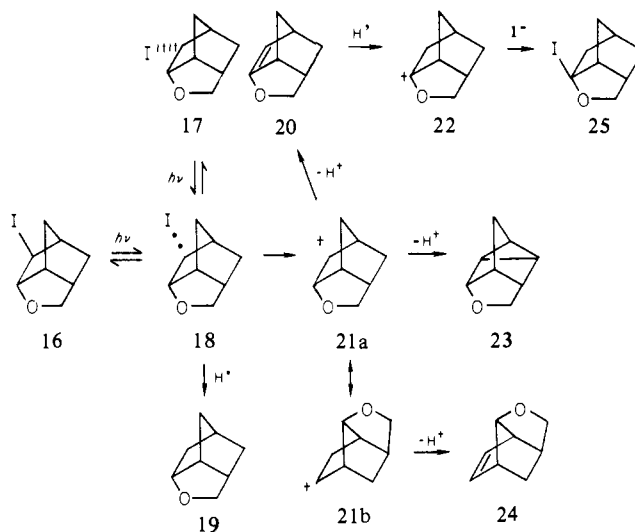
The results from irradiation of iodides 4, 7, and 10 are summarized in Table I. In each case, the ionic product 6, 9, or 12 was formed predominantly, along with a small amount of the reduction product 5, 8, or 11. Therefore, the ready generation of bridgehead carbocations is not limited to the bicyclo[2.2.1]heptyl system. As with the latter system, there was no detectable formation of products arising from isomerization to the more stable C-2 cation. Likewise, there was no detectable incorporation of deuterium when the irradiations were conducted in methanol-*d*, as would be expected from conversion of the initially formed cation to a propellane or bridgehead alkene intermediate.

Iodo Ether 16. Treatment of 5-bicyclo[2.2.1]heptene-2-endo-methanol (15) with iodine and triethylamine afforded an iodo ether, to which structure 16 is assigned based on the mechanism

Scheme III



Scheme IV

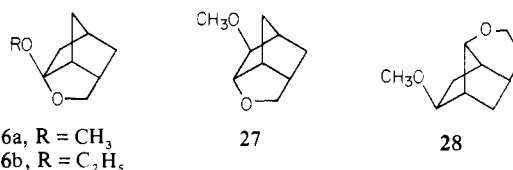
Table II. Irradiation of Iodo Ether 16^a

solvent	time, h	yield, % ^b								
		16	17	19	23	24	25	26	27	28
CH ₃ OH	2	<i>c</i>	<i>c</i>	8	19	6		11	6	11
(C ₂ H ₅) ₂ O	4	28	16	6	18	8	4		8	
C ₆ H ₆	2	15	11	8	15	1	11			
C ₆ H ₁₄	1	33	16	5	14	7	6			

^a Conducted as described in the Experimental Section at 254 nm on 0.05 M solutions. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. ^c Trace.

outlined in Scheme III.⁶ The presence of the tricyclic ring system of iodo ether 16 was verified by lithium aluminum hydride reduction to the previously known parent ether 19.⁸

The results from irradiation of iodo ether 16 (Scheme IV) in several solvents are summarized in Table II. Formed in each case were the epimeric endo iodide 17, the reduction product 19,⁸ and the elimination products 23^{7,9} and 24. In methanol the latter two products were accompanied by the corresponding ethers 27 and 28, as expected from competing deprotonation and nucleophilic trapping of cation 21.



As with the starting exo iodide 16, lithium aluminum hydride reduction of the endo isomer 17 afforded the parent ether 19,⁸ thereby confirming the basic tricyclic skeleton. The structural assignment 17 was confirmed by an analysis of the ¹H NMR spectrum (Table III), which showed that H-6 is coupled to both

(6) Preparation of iodo ether 16 in a similar fashion was subsequently reported, but with no accompanying detail; see: ref 7.

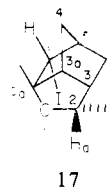
(7) Bruson, H. A.; Riener, T. W. U.S. Patent 2440220, 1948; *Chem. Abstr.* 1948, 42, 5471.

(8) Shono, T.; Ikeda, A.; Kimura, Y. *Tetrahedron Lett.* 1971, 3599-3602.

(9) Henshaw, B. C.; Rome, D. W.; Johnson, B. L. *Tetrahedron* 1971, 27, 2255-2269.

(4) Morita, K.; Kobayashi, T. *J. Org. Chem.* 1966, 31, 229-232. Suzuki, Z.; Morita, K. *Ibid.* 1967, 32, 31-34.

(5) Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* 1977, 99, 968-969.

Table III. Analysis of ¹H NMR Spectrum of Iodo Ether 17^a


chemical shift, δ	assignment	J , Hz							
		3	3a	5	6	6a	a	b	
4.19	6a		2.8		6.8				
3.96	6			4.6		6.8			
3.83	a	4.0							8.0
3.68	b								8.0
2.3 ^b	3a					2.8			4.0
2.4 ^c	3								4.0
2.5 ^d	5			4.6					

^a Based on double resonance experiments. ^b Part of unresolved multiplet; based on frequency required to decouple from 6a. ^c Part of unresolved multiplet; based on frequency required to decouple from a. ^d Part of unresolved multiplet; based on frequency required to decouple from 6.

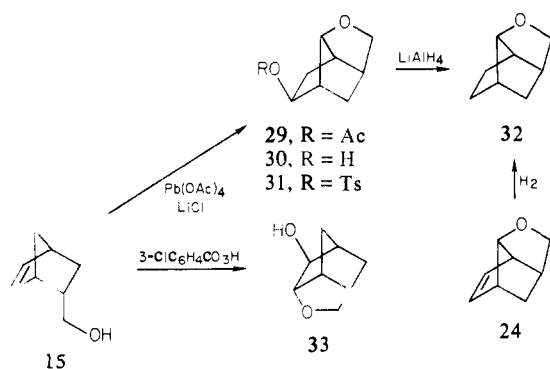
Table IV. Deuterium Labeling Studies^a

iodide	solvent	time, h	yield, % ^b						
			16	17	19	23	24	26b	
16	(C ₂ H ₅) ₂ O	2	17	6	11	18	7	11	
	(C ₂ H ₅) ₂ O/D ₂ O	1	c	c	24	27	8	5	
	(C ₂ H ₅) ₂ O/D ₂ O ^d	1	25	6	22	18	10	1	
					(43)	(0)	(0)	(80)	
								(79)	
16-d (96)	(C ₂ H ₅) ₂ O	2	15	7	10	18	7	10	
			(92)	(96)	(86)	(94)	(96)	(4)	

^a Unless otherwise indicated, irradiations were conducted as described in the Experimental Section on 0.05 M solutions contained in an air-cooled quartz tube suspended in front of a Hanovia 450-W mercury lamp equipped with a reflector. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Numbers in parentheses indicate percent *d*₁. ^c Trace. ^d Conducted at 254 nm.

H-6a and the bridgehead proton H-5.

Hydrogenation of the rearranged elimination product **24** afforded the dihydro derivative **32**, which was prepared independ-

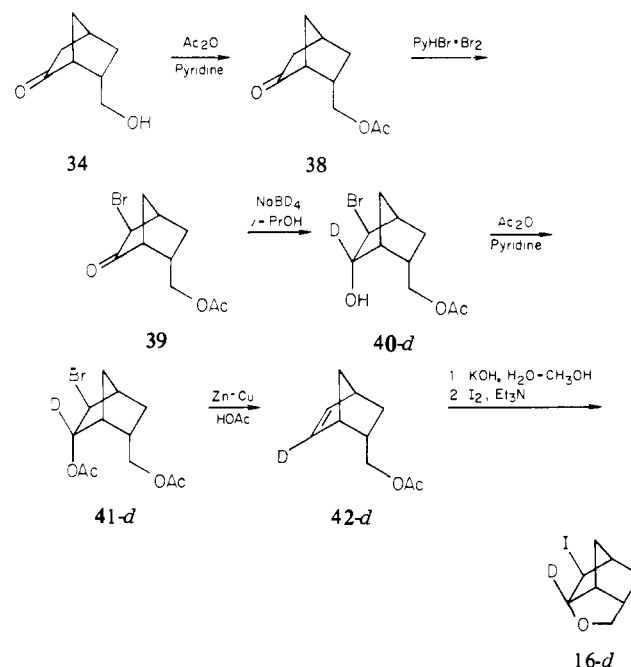


ently by treatment of the endo alcohol **15** with lead tetraacetate,¹⁰ followed by lithium aluminum hydride reduction of the resulting acetate **29**, conversion of the corresponding alcohol **30** to the tosylate **31**, and, once again, lithium aluminum hydride reduction. Photoether **27** was prepared independently by methylation of alcohol **33**, obtained by treatment of endo alcohol **15** with 3-chloroperoxybenzoic acid,¹¹ and the rearranged photoether **28** was

(10) See: Moriarty, R. M.; Gopal, H.; Walsh, H. G. *Tetrahedron Lett.* 1966, 4369-4374.

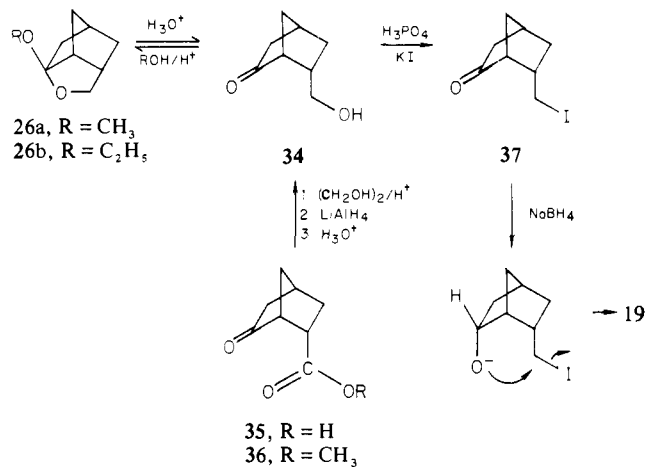
(11) Henbest, H. B.; Nicholls, B. *J. Chem. Soc.* 1959, 221-226.

Scheme V



prepared by methylation of alcohol **30**.

Also formed in each case was the rearranged iodide **25**, which was accompanied in methanol or diethyl ether by the corresponding ketal **26a** or **26b**. These latter products were characterized by hydrolysis to keto alcohol **34**, which was prepared independently from keto acid **35**.¹² Treatment of keto alcohol **34** with acidic

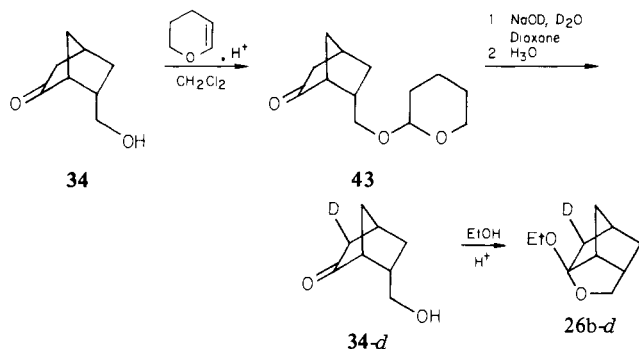


alcohol resulted in quantitative reversion to ketal **26a** or **26b**. However, attempted independent synthesis of the corresponding iodide **25** by treatment of keto alcohol **34** with hydrogen iodide afforded instead the iodo ketone **37**, the structure of which was confirmed by conversion to ether **19** on treatment with sodium borohydride.

Labeling and Trapping Studies. The rearranged iodide **25** and the ketals **26** apparently arise via trapping of cation **22**. However, labeling studies showed that this rearranged cation does not arise via a simple 1,2-hydride shift by the initially formed cation **21**. As seen in Table IV, irradiation of **16-d**, which was prepared as outlined in Scheme V, afforded ketal **26b** with substantial loss of deuterium, whereas the other photoproducts were all formed with little or no loss of deuterium. This result suggests that conversion of the initially formed cation **21** to the rearranged cation **22** involves deprotonation to the bridgehead alkene **20** followed by reprotonation. Such a mechanism was supported by the finding

(12) Beckmann, S.; Geiger, H. *Chem. Ber.* 1961, 94, 48-58. Beckmann, S.; Eder, G.; Geiger, H. *Ibid.* 1969, 102, 815-819.

Scheme VI

Table V. Irradiation of Iodo Ether 16 in the Presence of Furan^a

solvent	yield, % ^b						
	16	19	23	24	44	45	46
(C ₂ H ₅) ₂ O ^c	<i>d</i>	28	24	13	<i>e</i>	<i>d</i>	<i>e</i>
(C ₂ H ₅) ₂ O ^f	2	17	25	16	3	8	<i>e</i>
C ₆ H ₆ ^f	<i>e</i>	1	29	6	2	9	<i>e</i>
<i>g</i>	<i>e</i>	1	16	9	<i>d</i>	51	<i>e</i>
<i>g, h</i>	13	1	32	20	<i>e</i>	14	13

^a Conducted as described in the Experimental Section at 254 nm for 2 h on 0.05 M solutions of iodo ether 16 containing 1 mol equiv of triethylamine. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. ^c Contained 2 mol equiv of furan. ^d Trace. ^e None detectable. ^f Contained 24 mol equiv of furan. ^g Irradiation conducted in neat furan. ^h Triethylamine replaced by 1 mol equiv of 1-ethylsilatrane.

Table VI. Irradiation of Iodo Ether 25^a

solvent	time, h	yield, % ^b			
		25	19	26b	37
C ₆ H ₆ ^c	2	46	<i>d</i>	41	
(C ₂ H ₅) ₂ O ^e	1	20	4	37	17

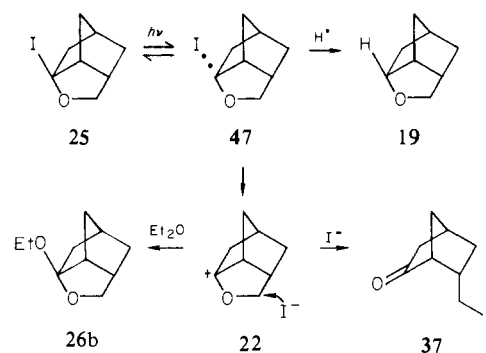
^a Conducted at 254 nm on 2-mL solutions as described in the Experimental Section. ^b Determined by gas chromatographic analysis relative to an internal hydrocarbon standard. ^c Conducted by using 26 mg of iodo ether 25. ^d Trace. ^e Conducted by using 18 mg of iodo ether 25.

that irradiation of unlabeled iodo ether 16 in diethyl ether saturated with deuterium oxide afforded ketal 26b with substantial incorporation of deuterium (Table IV).¹³ The fact that the resulting ketal 26b was specifically labeled in the 6-exo position, as expected from deuteration of the bridgehead alkene intermediate 20, was shown by independent synthesis (Scheme VI).

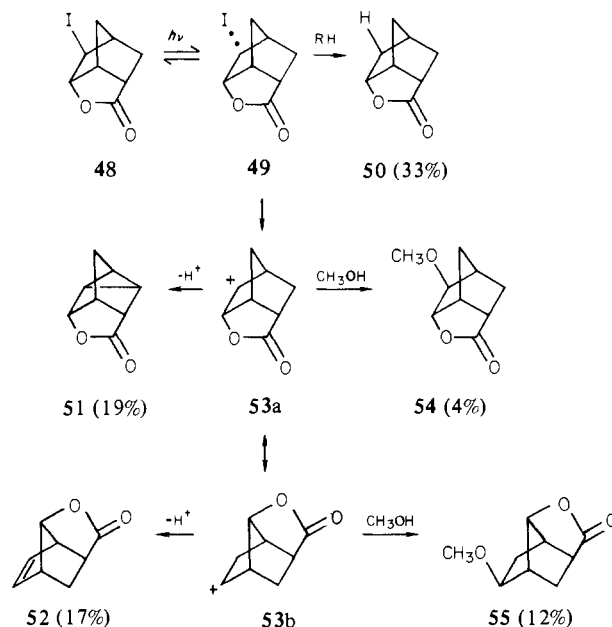
In further support for the involvement of the highly reactive bridgehead alkene 20 as an intermediate, it was found that irradiation of iodo ether 16 in the presence of furan afforded a small amount of a product having spectral properties consistent with those of the expected [4 + 2] adduct 44 (Table V). At least a moderate concentration of furan was required to effect trapping of the bridgehead alkene 20. However, going to furan as the solvent resulted in the predominant formation of adduct 45, which apparently arises from trapping of the initially formed radical 18 and/or cation 21.

(13) The accompanying incorporation of deuterium in the reduction product 19 is probably attributable to hydrogen iodide (or deuterium iodide) serving as a major source of hydrogen (or deuterium) atoms for the radical 18.

Scheme VII

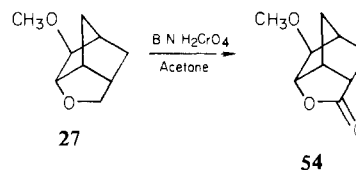


Scheme VIII



Iodo Ether 25. Irradiation of the rearranged iodo ether 25 in benzene afforded the iodo ketone 37 (Scheme VII and Table VI). In ether solution this product was accompanied by the ketal 26b.

Iodo Lactone 48. As shown in Scheme VIII, irradiation of the analogous iodo lactone 48¹⁴ in methanol afforded principally the reduction product 50,¹⁵ accompanied by the elimination products 51 and 52 and the ethers 54 and 55, the expected products from competing deprotonation and nucleophilic trapping of cation 53. The elimination products 51 and 52 were characterized by their spectroscopic properties and analogy with the related products obtained from iodo ether 16. Since ethers 54 and 55 could not



be distinguished spectroscopically, the former was prepared independently by oxidation of the corresponding photoether 27 obtained from iodo ether 16. There was no detectable formation of a photoproduct from iodo lactone 48 analogous to ketal 26a.¹⁶

(14) Singh, P.; Hodgson, D. J. *Acta Crystallogr., Sect. B* 1974, B30, 828-832, and references cited therein.

(15) Alder, K.; Diels, O. *Justus Liebigs Ann. Chem.* 1928, 460, 117. Alder, K.; Stein, G. *Ibid.* 1934, 514, 197.

(16) Contrary to previously reported irradiations in which zinc was used as a scavenger for hydrogen iodide,^{14,17} there was also no detectable fragmentation of iodo lactone 47 to 5-bicyclo[2.2.1]heptane-2-*endo*-carboxylic acid. This latter reaction is apparently a competing ground-state reaction involving zinc and photogenerated hydrogen iodide.

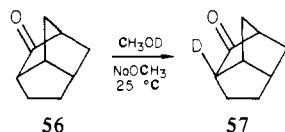
(17) Jones, T. H.; Kropp, P. J. *Org. Photochem. Synth.* 1976, 2, 82-84.

Discussion

The formation of ethers **6**, **9**, and **12** from the bridgehead iodides **4**, **7**, and **10** indicates that predominant cationic photobehavior is general for bridgehead systems and not limited to 1-bicyclo[2.2.1]heptyl derivatives. The enhanced ratio of ionic to radical products from iodides **4**, **7**, and **10** compared with iodide **1** probably reflects somewhat increased rates of electron transfer due to the greater stability of the resulting bridgehead cations compared with the 1-bicyclo[2.2.1]heptyl cation.

Predominant ionic photobehavior is exhibited also by iodo ether **16**. The elimination products **23** and **24** and the nucleophilic substitution products **27** and **28** are those expected from the corresponding cation **21**. On the other hand, the epimeric endo iodide **17** probably arises via recombination of the initially formed radical pair **18**, since nucleophilic trapping of 2-bicyclo[2.2.1]heptyl cations normally occurs from the exo side with high selectivity. Therefore, both the endo iodide **17** and the reduction product **19** are radical products.

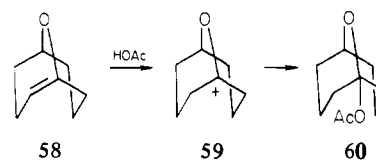
It is clear that iodo ether **16** amazingly undergoes, in addition, competing elimination to the bridgehead alkene **20**, a process apparently involving deprotonation of the carbocationic intermediate **21**.¹⁸ As noted in the introduction, it has previously been observed that carbocations generated by irradiation of alkyl iodides have a pronounced tendency to undergo deprotonation to afford unsaturated products.²⁴ This process is probably facilitated in the present case by the nearly parallel orientation of the C_{6a}-H bond of cation **21** and the adjacent vacant p orbital at C₆, just as the previously observed base-catalyzed exchange of deuterium in ketone **56**²³ is apparently facilitated by favorable overlap be-



tween the π orbitals of the carbonyl group and the adjacent filled p orbital of the corresponding carbanion. The failure of iodides **1**, **4**, **7**, and **10** to undergo analogous elimination to a bridgehead alkene is thus attributable, at least in part, to a lack of appropriate orbital overlap.²⁴

Once formed, the highly reactive bridgehead alkene **20** undergoes rapid reprotonation to afford not the original cation **21**, which surely shares some of the stability characteristic of 2-norbornyl cations, but rather the rearranged cation **22**, which is a bridgehead cation and is destabilized by the inductive electron withdrawal of the oxygen substituent.²⁵ Preferential formation

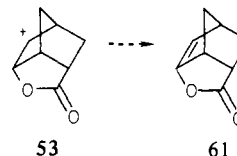
of this cation implies resonance stabilization by the adjacent oxygen substituent, despite the bridgehead position. Similar behavior is exhibited by the bridgehead alkene **58**, which undergoes preferential protonation to afford the bridgehead cation **59**.²⁶



The resulting rearranged cation **22** is sufficiently reactive that it undergoes nucleophilic trapping by diethyl ether, a property shared by other highly energetic bridgehead cations such as the 1-bicyclo[2.2.1]heptyl and 1-bicyclo[2.2.2]octyl cations. Trapping of **22** by iodide ion also occurs, yielding the rearranged iodo ether **25**, which, in turn, displays ionic photobehavior. The low yield of reduction product **19** upon irradiation of iodo ether **25** suggests that electron transfer to afford cation **22** occurs readily, another indication of the surprising stability of this bridgehead cation. Rearrangement of **25** to the iodo ketone **37** probably occurs as shown in Scheme VII; interestingly, such cleavages are common for α -halo ethers in the ground state.^{27,28} Indeed, iodo ether **25** is a member of a small class of stable compounds having geminal halogen and hetero atom substituents. In acyclic systems such compounds are generally unstable thermally by virtue of their ready ionization to afford halide ions and resonance-stabilized carbocations. Iodo ether **25**, however, is relatively stable thermally, although photochemically labile, since ionization requires formation of the bridgehead cation **22**, a process which does not occur easily in the ground state but proceeds readily upon irradiation.

In the presence of triethylamine as a scavenger for hydrogen iodide, the bridgehead alkene **20** could be trapped with furan to afford the [4 + 2] adduct **44**. In the presence of the weaker base 1-ethylsilatrane, however, preferential protonation of **20** occurred instead; the resulting cation **22** was trapped nucleophilically by furan to afford the adduct **46**.²⁹

In contrast with iodo ether **16**, the analogous iodo lactone **48** gave no detectable products attributable to the intermediacy of the bridgehead alkene **61**. The lack of deprotonation to **61** is



(18) (a) For a recent discussion of bridgehead alkenes and their properties, see: Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891-1900. (b) Although formation of the bridgehead alkene intermediate **20** is readily explained in terms of deprotonation of carbocation **21**, the available data are also consistent with an alternative, light-induced molecular elimination of hydrogen iodide directly from iodo ether **16**, a process which has been proposed for iodoethane in the gas¹⁹ and solid phases²⁰ and in argon matrix,²¹ but concerning which there has been much controversy.²² No examples of molecular elimination of hydrogen iodide in the solution phase have previously been reported. As can be seen from comparison of Tables II and IV, there was no observable effect of wavelength on either the rate of formation of ketal **26b** or on the extent of deuterium incorporation. Likewise, there was no detectable deuterium isotope effect on the rate of formation of **26b** from **16-d**.

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(24) Although conformationally labile, iodides **7** and **10** exist preferentially in the chair conformations shown, in which there is a poor overlap between the C₁ orbital and any of the adjacent C-H bonds.

(25) Competing reprotonation of **20** to re-form cation **21** as well as to form the rearranged cation **22** apparently does not occur, since formation of the unsaturated products **23** and **24** occurs with no detectable incorporation of deuterium on irradiation of iodo ether **16** in ether saturated with deuterium oxide (Table IV).

probably attributable to enhanced strain introduced by the presence of the carbonyl group. Again in contrast with iodo ether **16**, iodo lactone **48** afforded a substantially higher yield of the reduction product **50**. Therefore, electron transfer apparently occurs less efficiently in the lactone system, apparently attributable to destabilization of the cation **53** by the presence of the carbonyl group.

We continue to explore the intriguing and diverse photobehavior of alkyl halides.

Experimental Section

General Procedures. Infrared spectra were obtained on carbon tetrachloride solutions with a Beckman 4250 or Perkin-Elmer 421 grating spectrophotometer and ultraviolet spectra on ethanol solutions with a Cary 14 spectrophotometer. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected and uncalibrated. Mass spectra were obtained with an AEI MS-902 or Hitachi RMU-6E spec-

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(29) Alternatively the C_{6a} adduct **46** may arise, at least in part, as a secondary photoproduct from the rearranged iodo ether **25**.

trometer; m/e values reported include the parent ion peak and other significantly large peaks appearing above m/e 55. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument using 10-ft \times 0.125-in. stainless steel columns packed with either (A) 20% SF-96 or (B) 20% Carbowax 20M on 60–80 mesh Chromosorb W. Peak areas were obtained by the cut-and-weigh method and corrected for experimentally determined response factors. Preparative gas chromatography was carried out on a Varian Aerograph 90P or 920 instrument using 10-ft \times 0.25-in. stainless steel or nickel columns packed with the materials described above. Proton nuclear resonance spectra were obtained on chloroform- d solutions with a Varian XL-100 spectrometer or on carbon tetrachloride solutions with a JEOL C-60HL spectrometer; data are reported in the following manner: chemical shift (multiplicity, integration, coupling constant, and assignment). Multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br = broadened.

Irradiations. As indicated, irradiations were conducted under an atmosphere of nitrogen either at 254 nm by using a quartz vessel suspended in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 lamps or with the broad mercury spectrum by using a Hanovia 450-W medium-pressure mercury arc and either a water-cooled quartz immersion well or an Ace 7883 reflector and a quartz tube. After the irradiation had been completed, the solution was poured into 50 mL of water and extracted with a 100-mL portion of diethyl ether. The organic layer was washed consecutively with 25-mL portions each of 10% aqueous sodium thiosulfate solution, saturated sodium bicarbonate solution, and water. The combined aqueous washings were back-extracted with a 25-mL portion of diethyl ether. The combined organic phases were dried over 25 mL of saturated sodium chloride solution followed by anhydrous sodium sulfate and subsequently filtered. The solvent was removed by distillation through a Vigreux column.

1-Iodobicyclo[3.2.1]octane (7). A diethyl ether solution of diazomethane was added to a solution of 500 mg (3.20 mmol) of bicyclo[3.2.1]octane-1-carboxylic acid³⁰ and 10 mL of diethyl ether with stirring. After the yellow color had dissipated, an additional 50-mL portion of diethyl ether was added, and the solution was washed with a 25-mL portion of saturated sodium chloride solution. The organic layer was then dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford 400 mg (2.38 mmol, 74%) of 1-(methoxycarbonyl)-bicyclo[3.2.1]octane as a yellow oil: ν_{\max} 2940, 2867, 1734, 1459, 1436, 1286, 1267, 1234, 1216, 1190, 1180, 1141, 1081, and 1052 cm^{-1} ; $^1\text{H NMR}$ δ 3.68 (s, 3, $-\text{OCH}_3$); m/e 168.1152 (calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$, 168.1149), 125 (49), 109 (42), and 67 (28).

According to the procedure of Jung and Lyster,⁵ nitrogen was bubbled through a solution of 1.0 g (5.9 mmol) of the crude ester and 2.5 mL of carbon tetrachloride (previously stirred with aqueous potassium hydroxide, dried over calcium chloride, and distilled from phosphorus pentoxide) for 10 min in a 10-mL round-bottomed flask. The flask was sealed with a septum cap and a 2.2-mL (4.4 g, 22 mmol) portion of iodotrimethylsilane³¹ was added via syringe. This mixture was stirred for 3 days at 75 °C. After cooling, the solution was concentrated under reduced pressure with a vacuum pump. The crude acyl iodide was rapidly transferred to a 100-mL quartz flask containing 70 mL of dichloromethane (previously washed with sulfuric acid, neutralized, dried over calcium chloride, and distilled from phosphorus pentoxide), and the flask was placed in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 G8T5 lamps and a magnetic stirrer. An Alihn condenser sealed with a septum cap containing nitrogen inlet and outlet needles was inserted, and the solution was irradiated with stirring under a nitrogen atmosphere. Aliquots were quenched with ethanol, and after 8 h gas chromatographic analysis indicated that most of the acyl iodide had reacted. The resulting solution was washed consecutively with 25-mL portions each of water, 10% sodium thiosulfate solution, and saturated sodium bicarbonate solution. The aqueous washings were back-extracted with a 25-mL portion of dichloromethane. The combined organic layers were washed with a 25-mL portion of saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by distillation. Isolation by preparative gas chromatography afforded 200 mg (0.847 mmol, 14%) of iodide 7 as pale-yellow crystals having spectral properties identical with those previously reported.²

1-Iodobicyclo[3.3.1]nonane (10). Into a 25-mL Pyrex bomb tube were placed 1.0 g (5.1 mmol) of 1-(ethoxycarbonyl)bicyclo[3.3.1]nonane³² and 25 mL of purified carbon tetrachloride. After nitrogen was bubbled through the solution for 10 min, a septum cap was placed over the top

of the tube and a 2-mL (4 g, 20 mmol) portion of iodotrimethylsilane³¹ was added via syringe. The tube was then sealed and heated at 75 °C. After 3 days, the mixture was concentrated under reduced pressure with a vacuum pump. The residue was added to a 75-mL portion of purified dichloromethane in a 100-mL quartz flask and irradiated for 4 h at 254 nm as described above. Workup of the mixture as described above followed by isolation by preparative gas chromatography afforded 165 mg (0.656 mmol, 13%) of iodide 10 as a pale-yellow liquid: ν_{\max} 2954, 2869, 1457, 1364, 1301, 1258, and 1222 cm^{-1} ; lit.³³ no spectral data reported.

Irradiation of Iodides 4, 7, and 10. The irradiations described in Table I resulted in the isolation of the following products by preparative gas chromatography:

Bicyclo[2.2.2]octane (5) was identified by comparison of gas chromatographic retention times on columns A and B with those of a commercial sample.

1-Methoxybicyclo[2.2.2]octane (6, Y = OCH_3), 1-ethoxybicyclo[2.2.2]octane (6, Y = OC_2H_5), and 1-methoxybicyclo[3.2.1]octane (9) had spectral data identical with those previously reported.²

Bicyclo[3.2.1]octane (8) was isolated as a colorless solid: ν_{\max} 2930, 2868, 1461, 1217, and 1019 cm^{-1} ; lit.³⁴ ν_{\max} 2940 and 1470 cm^{-1} .

Bicyclo[3.3.1]nonane (11) was isolated as a colorless solid: ν_{\max} 2987, 2837, 1446, 1392, and 1136 cm^{-1} ; lit.³⁵ ν_{\max} 2975, 2900, 2845, and 1450 cm^{-1} .

1-Methoxybicyclo[3.3.1]nonane (12) was isolated as a colorless liquid: ν_{\max} 2924, 2848, 2816, 1466, 1402, 1351, 1177, 1068, 1048, 904, 895, and 851 cm^{-1} ; $^1\text{H NMR}$ δ 4.23 (s, 3, $-\text{OCH}_3$); lit.³³ no spectral data reported.

6-exo-Iodohexahydro-3,5-methano-2H-cyclopenta[b]furan (16). **A. Preparation.** A solution containing 50.0 g of a commercial specimen of 5-norbornene-2-methanol (15) (68:32 endo:exo; 0.277 mol endo), 100 g (0.394 mol) of iodine, 56.0 g (0.550 mol) of triethylamine, and 300 mL of methanol was heated under reflux for 48 h. After removal of the solvent under reduced pressure, 200 mL of ether and 200 mL of water were added to the reaction mixture; the aqueous phase was separated and back-extracted with 100 mL of ether. The combined ether portions were washed with 10% sodium thiosulfate solution and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. Distillation yielded 50.2 g (73% yield) of iodo ether 16 as a colorless liquid: bp 100 °C (5 mm); λ_{\max} 259 nm (ϵ 620); ν_{\max} 1140, 1055, and 938 cm^{-1} ; NMR τ 5.38 (d, J = 6.0 Hz, 1, CH-6n) and 6.42 (br s, 3, CH₂-2 and CH-6a); m/e 249.9850 (calcd for $\text{C}_8\text{H}_{11}\text{IO}$ 249.9856), 123 (100), 92 (45), and 69 (45).

B. Reduction. A solution containing 0.6 g (2 mmol) of iodo ether 16 and 0.15 g (4.4 mmol) of lithium aluminum hydride in 10 mL of ether was heated to reflux under a nitrogen atmosphere overnight. After the usual workup, gas chromatographic analysis (A/B) showed an absence of starting material and the presence of one product, whose retention time and infrared spectrum were identical with those of an authentic specimen of hexahydro-3,5-methano-2H-cyclopenta[b]furan (19).⁸

C. Irradiation. The irradiations described in Tables II and IV resulted in the isolation of the following products by preparative gas chromatography.

6-endo-Iodohexahydro-3,5-methano-2H-cyclopenta[b]furan (17) was obtained (B) as a pale yellow oil: ν_{\max} (neat) 1165, 1118, 1072, 1046, 1010, 970, 894, and 758 cm^{-1} ; m/e 249.9852 (16) (calcd for $\text{C}_8\text{H}_{11}\text{IO}$, 249.9857), 123 (100), 95 (15), 93 (42), and 79 (24).

8-Oxatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (23) was obtained (A) as a colorless oil: ν_{\max} 3060, 1044, 1024, 968, and 923 cm^{-1} ; $^1\text{H NMR}$ τ 5.88 (br d, J = 1.5 Hz, 1, CH-7x), 6.29 (d, J = 1 Hz, 2, CH₂-9), 7.69 (m, 1, CH-6), 8.10 (m, 1, CH-1), 8.34 (s, 2, CH₂-5), and 8.84 (s, 3, CH₂-3, -3, and -4); m/e 122.0748 (93) (calcd for C_8H_{10} , 122.0738), 91 (100), 79 (42), and 77 (59); lit.⁹ ν_{\max} 3060, 1043, 1023, and 923 cm^{-1} ; NMR τ 5.90 (br t, J = 1.5 Hz, 1), 6.31 (d, J = 1.5 Hz, 2), 7.70 (br s, 1), 8.11 (br s, 1), 8.34 (br s, 2), and 8.84 (br s, 3).

3,3a,6,6a-Tetrahydro-3,6-methano-2H-cyclopenta[b]furan (24) was obtained (B) as a colorless oil: ν_{\max} 3055, 1058, 1045, 910, 898, and 705 cm^{-1} ; NMR τ 3.98 (m, 1, CH-4), 4.25 (m, 1, CH-5), 6.06 (br s, 3, CH₂-2 and CH-6a), 7.25 (m, 2, CH-3a and -6), 8.00 (d, J = 7.5 Hz, 1, CH-3), and 8.40 (m, 1); m/e 122.0736 (67) (calcd for $\text{C}_8\text{H}_{10}\text{O}$, 122.0732), 93 (33), 92 (81), 91 (100), and 79 (53).

6a-Iodohexahydro-3,5-methano-2H-cyclopenta[b]furan (25) was isolated by silica gel chromatography of the products from irradiation of iodide 16 in benzene. Hexane elution followed by removal of the solvent afforded a slightly pink liquid: λ_{\max} 266 nm (ϵ 890); ν_{\max} (neat) 2962, 2879, 1258, 1176, 1143, 1064, 1015, 987, 961, and 930 cm^{-1} ; $^1\text{H NMR}$

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δ 3.90 (d of d, 1, $J = 8.2$ and 3.2 Hz, CH_a -2), 3.40 (d, 1, $J = 8.2$ Hz, CH_b -2), and 3.04 (m, 1); m/e 249.9859 (calcd for $\text{C}_8\text{H}_{11}\text{O}$, 249.9856), 123 (100), 93 (35), 79 (25), 77 (35), and 65 (20).

6a-Methoxyhexahydro-3,5-methano-2H-cyclopenta[b]furan (26a) was obtained as a colorless liquid: ν_{max} 1354, 1322, 1284, 1274, 1156, 1120, 1104, 1023, 1014, and 982 cm^{-1} ; $^1\text{H NMR}$ δ 3.76 (d of d, 1, $J = 8.0$ and 3.7 Hz, CH_a -2), 3.41 (d, 1, $J = 8.0$ Hz, CH_b -2) and 3.15 (s, 3, $-\text{OCH}_3$); m/e 154.0997 (100) (calcd for $\text{C}_9\text{H}_{14}\text{O}_2$, 154.0994), 139 (30), 125 (45), 111 (40), 99 (35), 81 (50), 80 (85), 79 (50), and 67 (40).

6a-Ethoxyhexahydro-3,5-methano-2H-cyclopenta[b]furan (26b) was obtained (B) as a colorless oil: ν_{max} 1323, 1285, 1274, 1230, 1195, 1180, 1155, 1122, 1103, 1070, 1035, and 982 cm^{-1} ; $^1\text{H NMR}$ τ 6.10 (d of d, $J = 8.2$ and 3.8 Hz, 1, CH_a -2b), 6.44 (q of d, $J = 7.0$ and 2.0 Hz, 2, $-\text{OCH}_2\text{CH}_3$), 6.48 (d, $J = 8.2$ Hz, 1, CH_a -2a), 8.18 (m, 1), 8.38 (d, $J = 3.8$ Hz, 1, CH_b -3), 8.51 (br s, 3), 8.79 (m, 1), and 8.86 (t, 3, $J = 7.0$ Hz, $-\text{OCH}_2\text{CH}_3$); m/e 168.1148 (60) (calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2$, 168.1150), 139 (90), 93 (65), and 79 (100).

6-exo-Methoxyhexahydro-3,5-methano-2H-cyclopenta[b]furan (27) and **5-exo-methoxy-3,6-methano-2H-cyclopenta[b]furan (28)** were obtained (B) as colorless liquids having infrared spectra identical with those of authentic specimens prepared independently as described below.

Reduction of Iodo Ether 17. A solution containing 81 mg (0.32 mmol) of iodo ether 17 and 25 mg (0.74 mmol) of lithium aluminum hydride in 5 mL of ether was heated to reflux under a nitrogen atmosphere overnight. After the usual workup, gas chromatographic analysis showed no remaining starting material and only one product, whose retention time and infrared spectrum were identical with those of ether 19.⁸

Hydrogenation of Photoether 24. A solution containing 15 mg (0.125 mmol) of ether 24 and 10 mg of 10% palladium on charcoal in 5 mL of absolute ethanol was stirred under an atmosphere of hydrogen. Absorption ceased at 1.03 molar equiv. After filtration and removal of solvent by distillation, gas chromatographic analysis showed no remaining starting material and only one product, whose retention time and infrared spectrum were identical with those of the specimen of ether 32 prepared as described below.

Acid-Catalyzed Hydrolysis of Ketal 26 (R = CH_3CH_2). A solution containing 50 mg (0.2 mmol) of photoketal 26b in 50 mL of 2 N sulfuric acid was stirred at room temperature for 2.5 h. After continuous extraction with ether for 48 h, the resulting ether solution was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Gas chromatographic analysis showed 73% conversion to a single product, mp 84–86 °C, whose infrared spectrum was identical with that of a specimen of keto alcohol 34 obtained as described below.

Independent Synthesis of Photoether 27. A solution of 750 mg (4.07 mmol) of 6-exo-hydroxyhexahydro-3,6-methano-2H-cyclopenta[b]furan (33)¹¹ in 20 mL of 1,2-dimethoxyethane contained in a three-necked flask equipped with a stirring bar, condenser, and nitrogen inlet tube was cooled in an ice bath, and 390 mg (16 mmol) of sodium hydride was slowly added under a stream of nitrogen. The resulting solution was stirred at room temperature for 1 h, after which 2.8 g (20 mmol) of methyl iodide was added. After 3 h, the contents of the flask were combined with ether, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Removal of the ether afforded 630 mg of a pale yellow oil, which gave one peak on gas chromatographic analysis. Distillation provided 330 mg (50% yield) of ether 27 as a pale yellow liquid: bp 49–51 °C (0.5 mm); ν_{max} 1460, 1444, 1362, 1356, 1181, 1142, 1098, 1066, 1030, 978, 941, 921, and 904 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 4.04 (d, 1, $J = 5.0$ Hz, CH_a -6a), 3.83 (d of d, 1, $J = 8.0$ and 3.8 Hz, CH_b -2), 3.66 (d, 1, $J = 8.0$ Hz, CH_c -2), 3.35 (s, 3, $-\text{OCH}_3$), and 3.01 (br s, 1, CH -6). Anal. ($\text{C}_9\text{H}_{14}\text{O}_2$) C, H.

Independent Synthesis of Photoether 28. A solution of 2 mg of alcohol 30, prepared as described below, in 1 mL of 1,2-dimethoxyethane was treated with an excess of sodium hydride, followed by methyl iodide, as described above for photoether 27, to afford photoether 28 as a colorless oil: ν_{max} 1360, 1299, 1203, 1186, 1163, 1094, 1073, 1056, 1038, and 923 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 4.41 (br m, 1), 3.84 (d of t, 1, $J = 2.1$ and 6.6 Hz, CH_a -2), 3.64 (d, 1, $J = 6.6$ Hz, CH_b -2), and 3.27 (s, 3, $-\text{OCH}_3$). Anal. ($\text{C}_9\text{H}_{14}\text{O}_2$) C, H.

Independent Synthesis of Ether 32. A. **5-exo-Acetoxyhexahydro-3,6-methano-2H-cyclopenta[b]furan (29).** To a stirred solution containing 5.0 g (4.0 mmol) of empirically pure 5-norbornene-2-endo-methanol (15) in 200 mL of dry benzene, that had been purged with nitrogen and maintained under a nitrogen atmosphere were added 18 g (430 mmol) of lithium chloride and 24 g (54 mmol) of lead tetraacetate, and the resulting mixture was heated to reflux for 12 h. After cooling, the mixture was filtered, and the filtrate washed successively with saturated sodium bicarbonate and saturated sodium chloride solutions and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the resulting viscous oil was subjected to column chromatography on 50 g of Woelm activity grade II alumina using

hexane as the eluant; the course of the separation was followed by gas chromatographic analysis. All fractions containing only the single, long-retention-time product were combined, and the solvent was removed under reduced pressure to afford 3.7 g (51% yield) of acetoxy ether 29 as a waxy solid: mp 46–48 °C; ν_{max} 1742, 1238, 1145, 1060, 1015, 940, and 900 cm^{-1} ; NMR τ 5.58 (m, 2, CH_a -5n and -6a), 6.42 (m, 2, CH_b -2), 7.80 (br s, 2, CH_c -3a and -6), and 8.10 (s, 3, $\text{CH}_3\text{C}(\text{O})$ -); m/e 182.0943 (5) (calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3$, 182.0943), 139 (21), 122 (100), 93 (66), and 79 (60).

B. **5-exo-Hydroxyhexahydro-3,6-methano-2H-cyclopenta[b]furan (30).** A solution containing 3.7 g (20 mmol) of acetoxy ether 29 and 1.2 g (33 mmol) of lithium aluminum hydride in 50 mL of diethyl ether was heated to reflux for 2 h. Following workup with water and dilute sodium hydroxide, gas chromatographic analysis showed no remaining starting material and the formation of only one product. Preparative gas chromatography afforded the alcohol 30 as a colorless, viscous oil: ν_{max} 3630, 3425, 1075, 1047, 998, 951, 932, 915, and 893 cm^{-1} ; NMR τ 5.62 (m, 1, CH_a -5n), 5.94 (s, 1, $-\text{OH}$), and 6.40 (br m, 3, CH_b -2 and -6a); m/e 140.0842 (2) (calcd for $\text{C}_8\text{H}_{12}\text{O}_2$, 140.0837), 122 (77), 93 (45), 92 (57), and 79 (100).

C. **Hexahydro-3,6-methano-2H-cyclopenta[b]furan (32).** Following the removal of solvent from the solution resulting from the lithium aluminum hydride reduction of acetoxy ether 29, 7 mL of pyridine and 5.0 g of *p*-toluenesulfonyl chloride were added, and the resulting mixture was maintained at -10 °C overnight. After the addition of 50 mL of ether, the mixture was washed successively with 30-mL portions of water, 10% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride and was dried over anhydrous sodium sulfate. The solution was then reduced in volume to approximately 20 mL and after nitrogen purge and the addition of excess (2.0 g) lithium aluminum hydride was heated to reflux for 2 h. After the usual workup, gas chromatographic analysis indicated the following components, which were identified by retention times and infrared spectra: alcohols 30 (8%) and 33 (18%) and ethers 19 (13%), 23 (36%), and 32 (20%). The last product was isolated by preparative gas chromatography as a colorless liquid: ν_{max} 1300, 1102, 1042, 950, 940, and 897 cm^{-1} ; $^1\text{H NMR}$ τ 6.05 (br s, 1, CH_a -6a), 6.51 (d of d, $J = 16.0$ and 6.4 Hz, 2, CH_b -2), and 7.87 (br s, 3, CH_c -3a, -3b, and -6); m/e 124.0896 (100) (calcd for $\text{C}_8\text{H}_{12}\text{O}$, 124.0888), 106 (13), 93 (75), 91 (47), and 82 (73).

Independent Synthesis of Keto Alcohol 34. A. **Methyl 6-Oxonorbornane-2-endo-carboxylate (36).** A solution of 3.5 g (23 mmol) of 6-oxonorbornane-2-endo-carboxylic acid (35)¹² in 50 mL of anhydrous ether was treated with an excess of ethereal diazomethane at room temperature. After the residual diazomethane had evaporated, the reaction mixture was dried over anhydrous sodium sulfate. Distillation yielded 3.0 g (78%) of ester 36 as a colorless liquid: bp 107–109 °C (6.0 mm); ν_{max} 1735 (br), 1432, 1347, 1297, 1190, 1172, 1070, and 1035 cm^{-1} ; $^1\text{H NMR}$ τ 6.43 (s, 3, $-\text{OCH}_3$), 7.00 (q, $J = 5.3$ Hz, 1, CH_a -2x), 7.32 (m, 2, CH_b -5), and 7.72 (br s, 1, CH -1); m/e 168.0784 (calcd for $\text{C}_9\text{H}_{12}\text{O}_3$, 168.0786), 140 (46), 137 (17), 108 (63), and 81 (100).

B. **Methyl 6-Oxonorbornane-2-endo-carboxylate 6-Ethylene Ketal.** A solution containing 1.26 g (7.5 mmol) of keto ester 36, 0.62 g (10 mmol) of ethane-1,2-diol, and a trace of *p*-toluenesulfonic acid in 10 mL of benzene was heated to reflux for 6 h in a flask equipped with a Dean-Stark water separator. After removal of solvent under reduced pressure, gas chromatographic analysis showed 92% conversion to a single product, which was isolated by preparative gas chromatography as a waxy solid: mp 52–53 °C (sealed capillary); ν_{max} 1735, 1434, 1340, 1250, 1190, 1105, 1062, 1022, and 960 cm^{-1} ; m/e 212.1044 (46) (calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$, 212.1049), 183 (6), 181 (12), 153 (100), and 126 (38).

C. **6-Oxonorbornane-2-endo-methanol (34).** A solution containing 1.2 g (5.6 mmol) of the above ketal in 20 mL of anhydrous ether was treated with an excess of lithium aluminum hydride and stirred under nitrogen for 4 h. After careful acidification with 10% hydrochloric acid, the ether was removed by distillation, and 10 mL of 10% hydrochloric acid was added to the reaction mixture. Following stirring for 3 h at room temperature, the mixture was continuously extracted with ether for 18 h. The ether extract was dried over anhydrous sodium sulfate, and the solvent was removed by distillation. Two sublimations under reduced pressure yielded 0.75 g (95%) of keto alcohol 34 as a waxy solid: mp 84–86 °C; ν_{max} 3590, 3380, 1745, 1323, 1127, 1055, 1002, and 980 cm^{-1} ; m/e 140.0839 (32) (calcd for $\text{C}_8\text{H}_{12}\text{O}_2$, 140.0837), 122 (20), 110 (30), and 80 (100).

6-endo-(Iodomethyl)-2-norbornanone (37). **Attempted Synthesis of Iodide 25.** The method of Stone and Schechter was employed in an attempt to prepare iodide 25 from alcohol 34.³⁶ A small, three-necked flask equipped with a nitrogen inlet tube, condenser, and stirring bar was

(36) Stone, H.; Schechter, H. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 543–544.

charged with 320 mg (2.50 mmol) of phosphorus pentoxide, 1.15 g (10.0 mmol) of 85% phosphoric acid, and 1.66 g (10.0 mmol) of potassium iodide. The resulting viscous mixture was stirred for several min, and 700 mg (5.00 mmol) of alcohol **34** was added. The temperature was raised by means of an oil bath to 80 °C for 12 h, during which time the color of the viscous mixture became deep red. Isolation of the product was accomplished by dissolving the reaction mixture in water and extracting with ether. The organic layer was washed successively with saturated sodium bicarbonate solution, 10% sodium thiosulfate solution, and saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the ether solution was distilled to afford 610 mg (2.44 mmol, 49%) of iodide **37**, which was found to be essentially pure by gas chromatographic analysis (B): ν_{\max} (CCl₄) 1744, 1406, 1293, 1198, 1175, 1137, and 936 cm⁻¹; ¹H NMR (CCl₄) δ 2.9 (m, 2, -CH₂I); *m/e* 249.9854 (50) (calcd for C₈H₁₁O, 249.9856), 123 (70), 95 (65), 81 (40), 79 (100), and 67 (60).

Treatment of iodide **37** with sodium borohydride in 2-propanol for 30 min at room temperature afforded ether **19** in 92% yield.

6-exo-Iodobexahydro-3,5-methano-2H-cyclopenta[b]furan-6a-d (16-d). **A. 2-endo-(Acetoxymethyl)-5-norbornene (42)**. A solution of 4.7 g (34 mmol) of keto alcohol **34** in 100 mL of pyridine and 50 mL of acetic anhydride was stirred overnight at room temperature. The solution was then poured over 200 g of ice and stirred 2 h, after which 500 mL of water was added, and the mixture was continuously extracted with pentane for 2 days. The pentane solution was distilled to afford 5.2 g (84%) of **6-endo-(acetoxymethyl)-2-norbornanone (38)** as a colorless liquid: bp 84–86 °C (0.1 mm); ν_{\max} (neat) 2958, 1745, 1365, 1235, and 1033 cm⁻¹; ¹H NMR (CCl₄) δ 3.77 (ABX, 2, *J*_{AB} = 15 Hz, *J*_{AX} = 7 Hz, *J*_{BX} = 6 Hz, -CH₂OAc) and 1.93 (s, 3, -OCH₃). Anal. (C₁₀H₁₄O₃) C, H.

Ketone **38** (364 mg, 2.00 mmol) was dissolved in 10 mL of acetic acid contained in a 25-mL, round-bottomed flask equipped with a stirring bar, condenser, and nitrogen inlet tube. Pyridinium hydrobromide perbromide (640 mg, 2.00 mmol) was added to the solution, the temperature was raised to 60 °C with an oil bath, and the solution was stirred overnight. After cooling, the acetic acid solution was dissolved in 100 mL of ether and washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. Drying of the ether solution over anhydrous sodium sulfate followed by removal of the solvent afforded 480 mg of a yellow oil, which was purified by Kugelrohr distillation at 100 °C (0.03 mm) to provide 380 mg (73%) of **6-endo-(acetoxymethyl)-3-exo-bromo-2-norbornanone (39)** as a slightly yellow liquid: ν_{\max} (neat) 2955, 1745, 1364, 1233, and 1032 cm⁻¹; ¹H NMR (CCl₄) δ 3.80 (m, 3, -OCH₂- and CH-3) and 1.95 (s, 3, -CH₃); *m/e* 260.0045 (calcd for C₁₀H₁₃BrO₃, 260.0048), 220 (70), 218 (70), 139 (20), 122 (20), 95 (30), 93 (80), 91 (30), 85 (70), and 83 (100).

Care was exercised to exclude moisture from the reaction to avoid hydrolysis of the acetate under the following reaction conditions. A 100-mL, three-necked flask containing a stirring bar was oven-dried and cooled under nitrogen. A solution of 1.04 g (4.00 mmol) of bromo ketone **39** in 30 mL of 2-propanol, which had been dried by distillation from magnesium iodide, was introduced into the flask under a stream of nitrogen. The solution was cooled in an ice bath, 76 mg (2.0 mmol) of sodium borohydride was added, and the resulting mixture was stirred for 2 h. Excess sodium borohydride was destroyed with 10% hydrochloric acid, and the solution was transferred to a continuous extractor with 300 mL of water and extracted with ether for 24 h. The ether extract was dried with saturated sodium chloride solution and anhydrous sodium sulfate. Evaporation of the ether followed by chromatography on silica gel afforded 680 mg (64%) of **6-endo-(acetoxymethyl)-3-exo-bromo-2-endo-norbornanol (40)** as a yellow oil: ν_{\max} (neat) 3450, 2960, 1733, 1708, 1445, 1364, 1245, 1059, and 1025 cm⁻¹; ¹H NMR (CDCl₃) δ 3.7 (m, 4, CH-2, CH-3, and -CH₂O-), 2.80 (br s, 1, -OH), and 2.01 (s, 3, -COCH₃).

Bromohydrin **40** (150 mg, 0.570 mmol) was dissolved in 10 mL of acetic acid under nitrogen. Freshly prepared zinc-copper couple (300 mg) was added and the mixture was stirred and maintained under reflux for 9 h, during which time the metal turned from black to red-brown. The mixture was cooled and filtered into a separatory funnel, 100 mL of water was added, and the solution was extracted with three 15-mL portions of ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and saturated sodium chloride solution and dried over anhydrous sodium sulfate. Removal of the solvent followed by silica gel chromatography and preparative gas chromatography (B) afforded 20 mg (21%) of **2-endo-(acetoxymethyl)-5-norbornene (42)**¹¹ as a colorless liquid: ν_{\max} (CCl₄) 3059, 2960, 2870, 1739, 1443, 1363, 1227, and 1026 cm⁻¹; ¹H NMR (CDCl₃) δ 6.03 (d of d, 1, *J* = 5.5 and 3.0 Hz, CH-5), 5.81 (d of d, 1, *J* = 5.5 and 2.5 Hz, CH-6), 3.61 (ABX, 2, *J* = 11, 8, and 7 Hz, -CH₂O-), 2.80 (br s, 2, CH-1 and -4), 1.95 (s, 3, -COCH₃), and 0.54 (m, 1, CH_{en}-3).

B. 2-endo-(Acetoxymethyl)-5-norbornene-6-d (42-d). The labeled acetate was prepared by a modification of the procedures described above and with out isolation of intermediates in order to improve the overall yield. The ketone **39** (4.05 g, 15.5 mmol) was dissolved in 120 mL of 2-propanol in a flask protected from moisture by a flow of dry nitrogen. The solution was cooled in an ice bath, 400 mg (9.5 mmol) of sodium borodeuteride (Merck) was added, and the resulting solution was stirred for 4 h at 0 °C and 1 h at room temperature. The excess sodium borodeuteride was destroyed with 10% hydrochloric acid, and the contents of the flask were continuously extracted with ether.

After removal of the ether, the residue was treated with acetic anhydride-pyridine solution to afford 4.18 g of crude diacetate **41-d**, which was then dissolved in 200 mL of acetic acid contained in a flask fitted with a condenser and nitrogen inlet tube. With stirring, 4 g of zinc-copper couple was added, and the resulting mixture was brought to reflux. After 4 h, the mixture was filtered into a separatory funnel, water was added, and the solution was extracted several times with ether. The ether was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution, followed by drying over anhydrous sodium sulfate. Removal of the solvent and chromatography on silica gel afforded 1.65 g (9.30 mmol) of deuterated acetate **42-d** in 60% overall yield from ketone **39**: ¹H NMR (CCl₄) δ 6.00 (d, 1, *J* = 3.0 Hz, CH-5).

C. Iodo Ether 16-d. Acetate **42-d** (1.65 g, 9.30 mmol) was treated at room temperature for 2 h with a solution of 2 g of potassium hydroxide in 60 mL of aqueous methanol (1:5). The solution was neutralized with 10% hydrochloric acid, diluted with water, and continuously extracted with ether. The ether was dried and distilled, and the residue was taken up in 12 mL of methanol under a nitrogen atmosphere. To this solution were added 3.00 g (12.6 mmol) of iodine and 2.0 mL (1.5 g, 14 mmol) of triethylamine, and the resulting solution was brought to reflux. After 40 h, 120 mL of ether was added, and the precipitate that formed was removed by filtration. The ether was washed with water, 10% sodium thiosulfate solution, saturated sodium bicarbonate solution, and saturated sodium chloride solution. Drying of the ether solution over anhydrous sodium sulfate was followed by distillation and chromatography of the residue on silica gel. Elution with pentane afforded 1.54 g (65%) of deuterated iodide **16-d** as a yellow oil: ¹H NMR (CCl₄) δ 3.56 (m, 3, CH₂-3 and CH-6); deuterium analysis: 4% *d*₀, 96% *d*₁.

Independent Synthesis of 6a-Ethoxyhexahydro-3,5-methano-2H-cyclopenta[b]furan-6-exo-d (26b-d). Alcohol **34** (560 mg, 4.00 mmol) was dissolved in 20 mL of dry dichloromethane contained in a 50-mL, round-bottomed flask. To the solution was added 1.64 g (20.0 mmol) of dihydropyran (freshly distilled from lithium aluminum hydride) and a trace of *p*-toluenesulfonic acid. The solution was stirred under a dry atmosphere for 3 h at room temperature, transferred to a separatory funnel, washed with 0.5 M sodium hydroxide solution and saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The dichloromethane was removed, and the crude tetrahydropyranyl ether **43** was subjected to deuterium exchange without purification according to the procedure of Meinwald et al.³⁷

Compound **43** was added to a solution of 15 mL of dioxane and 15 mL of deuterium oxide in which a small piece of sodium had been dissolved. This solution was stirred at room temperature overnight under a nitrogen atmosphere and then acidified with 3 mL of concentrated hydrochloric acid and stirred for 1 h. The resulting solution was neutralized with saturated sodium bicarbonate solution and extracted several times with ether. After the ether solution had been dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, the solvent was removed by rotary evaporation.

The resulting crude deuterated alcohol **34-d** was taken up in 30 mL of ethanol, a trace of *p*-toluenesulfonic acid was added, and this solution was stirred at room temperature overnight and then heated to reflux for 1 h. Water was added, and the solution was extracted several times with pentane. The combined pentane extracts were concentrated by distillation, and the product was collected by preparative gas chromatography (A) to afford 180 mg (27%) of a colorless liquid having a ¹H NMR spectrum essentially identical with that of acetal **26b-d** obtained from irradiation of iodo ether **16** in ether-deuterium oxide solution. Deuterium analysis: 12% *d*₀, 71% *d*₁, and 17% *d*₂.

Trapping of Bridgehead Alkene 20. From the irradiation of iodo ether **16** as described in Table V, the following products were isolated by preparative gas chromatography (A and B). Ethers **19**, **23**, and **24** were obtained as colorless liquids having spectral data in agreement with those reported above.

1,2,3,4,5,8-Hexahydro-5,8-epoxy-8a,2-epoxymethano-1,4-methano-4aH-naphthalene (44) was isolated as a colorless liquid: ν_{\max} (CCl₄) 3075, 2955, 2878, 1350, 1305, 1249, 1203, 1147, 1122, 1053, 1044, 1001,

(37) Thomas, A. F.; Schneider, R. A.; Meinwald, J. J. *Am. Chem. Soc.* **1967**, *89*, 68–70.

921, and 903 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 6.52 (d of d of d, $J = 7.5, 6.0$, and 1.5 Hz, CH-6 and CH-7), 4.72 (d, 2, $J = 6.0$ Hz, CH-5 and CH-8), 3.97 (d of d, 1, $J = 5.0$ and 8.5 Hz, CH_2 -10), 3.58 (d, 1, $J = 8.5$ Hz, CHb-10), and 2.3 (m, 4, CH-1, CH-2, CH-4, and CH-4a); m/e 190.0993 (25) (calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$, 190.0994), 162 (55), 149 (15), 132 (15), 121 (20), 107 (35), 94 (30), 91 (40), 81 (35), 79 (100), 77 (40), and 66 (30).

6-exo-(2-Furyl)hexahydro-3,5-methano-2H-cyclopenta[b]furan (45) was isolated as a colorless liquid: ν_{max} (CCl_4) 3121, 2965, 2873, 1585, 1500, 1283, 1148, 1080, 1059, 1022, 1011, 957, and 942 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.32 (m, 1, ArH-5'), 6.30 (d of d, 1, $J = 3.1$ and 1.9 Hz, ArH-4'), 6.00 (d, 1, $J = 3.1$ Hz, ArH-3'), 4.48 (d, 1, $J = 5.0$ Hz, CH-6a), 3.92 (d of d, 1, $J = 8.1$ and 4.2 Hz, CH_2 -2), and 3.76 (d, 1, $J = 8.1$ Hz, CHb-2); m/e 190.0996 (50) (calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$, 190.0994), 132 (100), 94 (40), 91 (45), 81 (60), 79 (75), 77 (60), and 69 (30).

6a-(2-Furyl)hexahydro-3,5-methano-2H-cyclopenta[b]furan (46) was isolated as a colorless liquid: ν_{max} (CCl_4) 2968, 2873, 1325, 1292, 1156, 1140, 1074, 1003, and 908 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.39 (br, 1, ArH-5'), 6.33 (d of d, 1, $J = 2.0$ and 3.0 Hz, ArH-4'), 6.23 (d, 1, $J = 3.0$ Hz, ArH-3'), 4.04 (d of d, 1, $J = 4.2$ and 8.0 Hz, CH_2 -2), and 3.76 (d, 1, $J = 8.0$ Hz, CHb-2); m/e 190.0996 (65) (calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$, 190.0994), 161 (100), 160 (85), 147 (25), 135 (30), 95 (90), 91 (35), 81 (25), 79 (35), and 77 (35).

Irradiation of 6-exo-Iodohexahydro-3,5-methano-2H-cyclopenta[b]furan-2-one (48). A solution of 265 mg of iodolactone 48¹⁴ in 20 mL of methanol was irradiated for 4 h at 254 nm. The results are summarized in Scheme VIII. Removal of solvent by distillation, followed by isolation using preparative gas chromatography, afforded the following products:

Hexahydro-3,5-methano-2H-cyclopenta[b]furan-2-one (50) was obtained as a waxy, colorless solid that was identical in every respect with an authentic specimen.¹⁵

8-Oxatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-9-one (51) was obtained (A) as a colorless oil: λ_{max} 3075, 3010, 1800, 1337, 1308, 1149, 1010, 1000, 992 and 978 cm^{-1} ; $^1\text{H NMR}$ τ 5.33 (m, 1), 7.42 (br s, 2), and 8.24 (s, 5); m/e 136.0508 (22) (calcd for $\text{C}_8\text{H}_8\text{O}_2$, 136.0524), 92 (60), 91 (100), 79 (52), 77 (26), and 66 (34).

3,3a,6,6a-Tetrahydro-3,6-methano-2H-cyclopenta[b]furan-2-one (52) was obtained (B) as a colorless oil: ν_{max} 3080, 1800, 1332, 1173, 1027, 1000, 748 and 718 cm^{-1} ; $^1\text{H NMR}$ τ 3.68 and 4.33 (2m, 2, CH-4 and -5), 5.73 (br s, 1, CH-6a), 6.81 (m, 1, CH-6), 7.25 (m, 1, CH-3a), 7.63 (br d, $J = 7.0$ Hz, 1, CH-3), 8.20 and 8.73 (2d of d, $J = 10.5$ and 5.0 Hz, 2, CH_2 -7); m/e 136.0523 (4) (calcd for $\text{C}_8\text{H}_8\text{O}_2$, 136.0524), 92 (25), 79 (100), and 77 (27).

6-exo-Methoxyhexahydro-3,5-methano-2H-cyclopenta[b]furan-2-one (54) was obtained as a colorless liquid having an infrared spectrum identical with that of a sample prepared independently as described below: ν_{max} (CCl_4) 1791, 1339, 1176, 1130, 1098, 1038, and 1019 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 4.28 (d, 1, $J = 5.0$ Hz, CH-6a), 3.36 (s, 3, $-\text{OCH}_3$), 3.2 (m, 2, CH-3 and CH-6), and 2.5 (m, 2, CH-3a and CH-5); m/e

168.0784 (30) (calcd for $\text{C}_9\text{H}_{12}\text{O}_3$, 168.0786), 140 (35), 80 (35), and 71 (100).

5-exo-Methoxyhexahydro-3,6-methano-2H-cyclopenta[b]furan-2-one (55) was obtained as a colorless liquid: ν_{max} (CCl_4) 1792, 1342, 1307, 1213, 1162, 1131, 1107, 1028, 1004, 951, and 931 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 4.96 (br, 1, CH-6a), 3.53 (d, 1, $J = 6.0$ Hz, CH-5), 3.29 (s, 3, $-\text{OCH}_3$), and 2.66 (m, 3, CH-3, CH-3a, and CH-6); m/e 168.0784 (calcd for $\text{C}_9\text{H}_{12}\text{O}_3$, 168.0786), 136 (60), 108 (40), 92 (55), 80 (50), 79 (100), and 66 (30).

Independent Synthesis of Lactone 54. A solution of 155 mg (1.01 mmol) of ether 27 in 10 mL of acetone was treated with excess 8 N chromic acid³⁸ at room temperature under a nitrogen atmosphere.¹¹ After 10 days of stirring, the green solids were removed by filtration and washed with acetone. The filtrate was dissolved in 50 mL of ether, and the solution was washed with saturated sodium bicarbonate and saturated sodium chloride solutions and dried over anhydrous sodium sulfate. Removal of the solvent afforded 110 mg of a viscous yellow liquid, which was purified by Kugelrohr distillation at 80–120 $^\circ\text{C}$ (0.1 mm) to give 90 mg (54% yield) of lactone 54 as a colorless liquid having an infrared spectrum identical with that of material obtained from irradiation of iodolactone 48 in methanol.

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Registry No. 4, 931-98-6; 5, 280-33-1; 6 (Y = OCH_3), 7697-14-5; 6 (Y = OC_2H_5), 49576-41-2; 7, 61192-26-5; 8, 6221-55-2; 9, 61192-23-2; 10, 63160-85-0; 11, 280-65-9; 12, 63160-90-7; *endo*-15, 15507-06-9; *exo*-15, 13360-81-1; 16, 42464-05-1; 16-*d*, 81523-23-1; 17, 81571-06-4; 19, 3354-68-5; 20, 81523-24-2; 23, 33237-15-9; 24, 81523-25-3; 25, 81523-26-4; 26a, 22532-37-2; 26b, 81523-27-5; 26b-*d*, 81523-28-6; 27, 33892-28-3; 28, 81523-29-7; 29, 35359-71-8; 30, 81523-30-0; 32, 27867-33-0; 33, 18684-64-5; 34, 81523-31-1; 34-*d*, 81523-32-2; 35, 42392-37-0; 36, 70680-88-5; 37, 81523-33-3; 38, 81523-34-4; 39, 81523-35-5; 40, 81523-36-6; 41-*d*, 81523-37-7; 42, 16053-06-8; 42-*d*, 81523-38-8; 43, 81523-39-9; 44, 81523-40-2; 45, 81523-41-3; 46, 81523-42-4; 48, 7732-50-5; 50, 6712-12-5; 51, 6169-95-5; 52, 81523-43-5; 54, 81523-44-6; 55, 81523-45-7; bicyclo[3.2.1]octane-1-carboxylic acid, 2534-83-0; 1-(methoxycarbonyl)bicyclo[3.2.1]octane, 81523-46-8; 1-(ethoxycarbonyl)bicyclo[3.2.1]octane, 81523-47-9; methyl 6-oxononan-2-*endo*-carboxylate 6-ethylene ketal, 70600-43- ∞ 0.

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Stereospecificity of the Oxymetalation of Optically Active 1,2-Cyclonadiene

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Abstract: The absolute configuration of (–)-1,2-cyclonadiene was established as *S*. The absolute configurations of (+)-(*Z*)-3-hydroxy-, alkoxy-, and acetoxy-cyclonadiene were assigned the *S* configuration on the basis of the silver ion induced solvolysis of optically active 9,9-dibromo-(*E*)-bicyclo[6.1.0]nonane of known stereochemistry. The stereospecificity of antarafacial oxymercuration and oxythallation of (–)-1,2-cyclonadiene has been determined by NMR techniques to be a function of the ligand on the metal. The stereospecificity of suprafacial acetoxyplumbation of (–)-1,2-cyclonadiene was shown to be 56%.

The generally accepted mechanism for the oxymercuration of an alkene involves a bridged or π -complexed mercurinium ion intermediate.¹ This reaction was initially extended to include allenes by Gardner, who elucidated the structures of the oxy-

mercurials derived from addition of mercuric acetate to 1,2-cyclonadiene, to 1,2,6-cyclonatriene, and to 2,3-pentadiene in ethanol.² Waters and Kiefer invoked the intermediacy of a σ -bridged intermediate in the methoxymercuration of a series of

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