J. Am. Chem. Soc. 1983, 105, 6907-6915

simultaneously through uranium glass for 6 h. In another experiment two solutions in benzene containing **1** (0.06 M) and **2** (0.058, 0.293 M) were similarly irradiated. Product analysis on column B gave the results shown in Figure 3.

Acknowledgment. Financial support for research in New York was provided by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society; for research in Hamburg by Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Konrad-Adenauer-Stiftung through a fellowship to C.S.; and for both laboratories by NATO. We thank Phyllis Wilson and Eric Orava for technical assistance, S. T. Bella for microanalyses, and Prof. David Cowburn and Mr. Francis Picart for the NOE experiment.

Registry No. **1**, 7299-55-0; **2**, 563-79-1; **4**, 80992-46-7; (*Z*)-**7a**, 87337-54-0; (*E*)-**8a**, 87337-55-1; **10a**, 87337-56-2; **10b**, 87337-58-4; **11**, 87337-60-8; **13a**, 87337-57-3; **13b**, 87337-59-5; **14**, 87337-61-9; **15a**, 71932-99-5; (*Z*)-**15b**, 87337-69-7; **17**, 17475-11-5; (*Z*)-**18**, 63281-98-1; **19**, 19115-28-7; **20a**, 87337-66-4; (*Z*)-**20b**, 87337-73-3; **21a**, 87337-65-3; (*E*,*Z*)-**21b**, 87337-71-1; (*Z*,*Z*)-**21b**, 87337-72-2; **22**, 87337-74-4; **25**, 87337-67-5; **26**, 87337-75-5; i, 87337-62-0; ii, 87337-63-1; iii, 87337-64-2; allyl bromide, 106-95-6; 1-(trimethylsilyl)propyne, 6224-91-5; pivaloyl chloride, 3282-30-2; (*Z*)-4-hexen-1-ol, 928-91-6; (*Z*)-4-hexen-1-ol tosylate, 87337-68-6; (*Z*)-2,2-dimethylundeca-9-ene-4-yne-3-ol, 87337-70-0; 1,1,1-trifluoro-3-decyn-2-one, 85336-10-3.

Photochemistry of Alkyl Halides. 10. Vinyl Halides and Vinylidene Dihalides[1]

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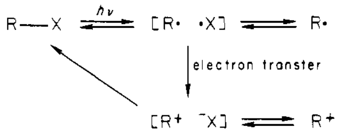
Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received October 14, 1982*

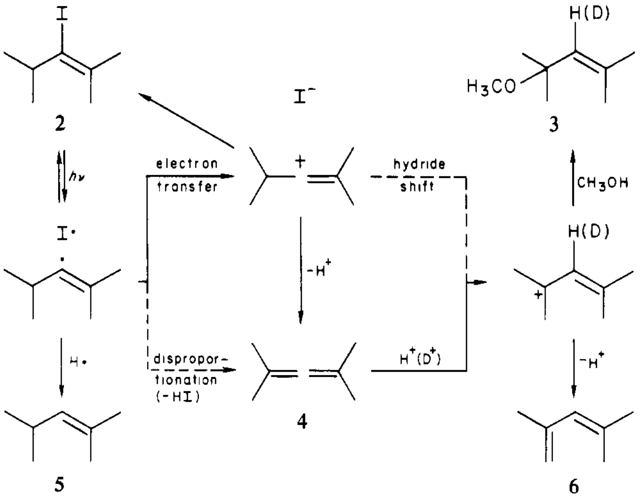
Abstract: The photobehavior of the acyclic vinyl iodide **2**, the 1-iodocycloalkenes **11–14** and **39**, the (halomethylene)cycloalkanes **45–48**, and the (dihalomethylene)cyclohexanes **62–64** has been studied. Except for the dichloride **64**, which exhibited only radical behavior, each of the halides afforded a mixture of ionic and radical products. The two bromides studied, **48** and **63**, afforded lower ratios of ionic to radical products than the corresponding iodides **45** and **62**. Irradiation of vinyl iodides was found to be a convenient and powerful method for the generation of vinyl cations, including the highly strained 1-cyclohexenyl and 1-cyclopentenyl cations and the unstabilized α-unsubstituted cations **51** and **54**. The latter cations underwent rearrangement to the ring-expanded 1-cycloalkenyl cations **28** and **36**, respectively. Lowering the temperature of the irradiation of iodides **13**, **14**, and **45** resulted in an increased ratio of ionic to radical products. However, iodide **47**, which underwent principally fragmentation to enyne **61**, showed little temperature effect.

It has long been known that absorption of light by alkyl halides generally results initially in homolytic cleavage of the carbon–halogen bond.[2] Recent studies in these laboratories have shown that in solution alkyl halides, particularly iodides, frequently afford photoproducts that are clearly derived from carbocationic intermediates, which we have suggested arise via electron transfer within the initially formed caged radical pair (Scheme I).[3,4] Irradiation of alkyl halides has proven to be not only a convenient but also a powerful method for the generation of carbocationic intermediates—including such difficultly formed ions as primary carbocations and the 1-norbornyl bridgehead cation.[3] We wish to report here the extension of this method to the generation of alkylvinyl cations, another class of carbocationic intermediates not easily generated by traditional ground-state methods.[5,7]

Scheme I



Scheme II



Results

Iodide 2. The acyclic vinyl iodide **2**[8] was prepared from ketone **1** by the general method of Pross and Sternhell.[9] In keeping with

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(1) Part 9: Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *47*, 2084–2090.

(2) For a review of the photobehavior of alkyl halides prior to our studies, see: Sammes, J. P. "Chemistry of the Carbon–Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(3) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135–8144.

(4) A number of reports have appeared concerning the photosolvolysis of benzyl halides: (a) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1962**, *85*, 915–922. (b) Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR* (*Engl. Transl.*) **1973**, *9*, 345–347. (c) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105–2108. (d) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 87–90. (e) Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625–4627. (f) Cristol, S. J.; Bindel, T. H. *Ibid.* **1981**, *103*, 7287–7293. These systems display photobehavior that differs substantially from that of alkyl analogues and, at least in part, apparently follows different mechanistic pathways.

(5) Solvolytic generation of alkylvinyl cations from vinyl precursors requires leaving groups having high nucleofugacity, such as the so-called super leaving groups CF_3SO_3 (triflate) and $C_4F_9SO_3$ (nonaflate); see ref 6.

(6) For a recent review of vinyl cations, see: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

(7) For a preliminary report of the present work, see: McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319–4320.

(8) Byrd, L. R.; Caserio, M. C. *J. Org. Chem.* **1972**, *37*, 3881–3891.

(9) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989–1003. See: Barton, D. H. R.; O'Brien, R. E.; Sternhell, S. *J. Chem. Soc.* **1962**, 470–475.

0002-7863/83/1505-6907$01.50/0

Table I. Irradiation of 2,4-Dimethyl-3-iodo-2-pentane (**2**)[a]

		yield,[b] %			
solvent	time, h	**2**	**3**	**5**	**6**
CH_3OH	2	35	14	11	22
	4	*c*	22	16	25
$CH_3OH^{e,f}$	1		37		44
	g		43		51
$CH_3OH^{e,h}$	1		12		15
CH_3OD	4	*d*	30[i]	64	*d*
CH_2Cl_2[j]	4	11		35	30
C_5H_{11}[j]	4	8		49	34

[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradition mixture. [c] Trace. [d] None detected. [e] Control experiment in which iodide **2** was replaced by an equivalent amount of ethyl iodide. [f] 1 molar equiv of allene **4** was added to the irradiation mixture before irradiation was initiated; 16% remained after 1 h. [g] Analysis of the reaction mixture after standing in the dark for 1 h. [h] Contained 1 molar equiv of diene **6**. [i] 72% d_1, 28% d_0. [j] 2 molar equiv of 1-ethylsilatrane present.

Table II. Irradiation of 1-Iodocyclooctene (**11**)[a]

		yield,[b] %						
solvent	time, h	**11**	**17**	**20**	**21**	**22**	**23**	**7**
CH_3OH	10	*c*	30	4	6	32	2	16
CH_2Cl_2	10	*c*		45	15	10		

[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Trace.

Scheme III

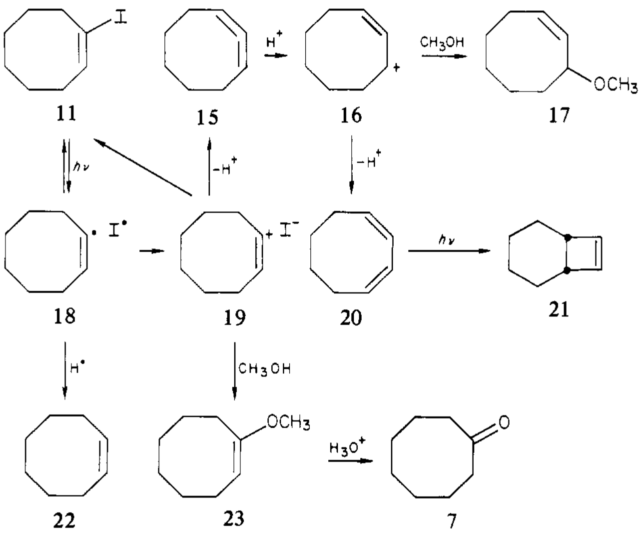
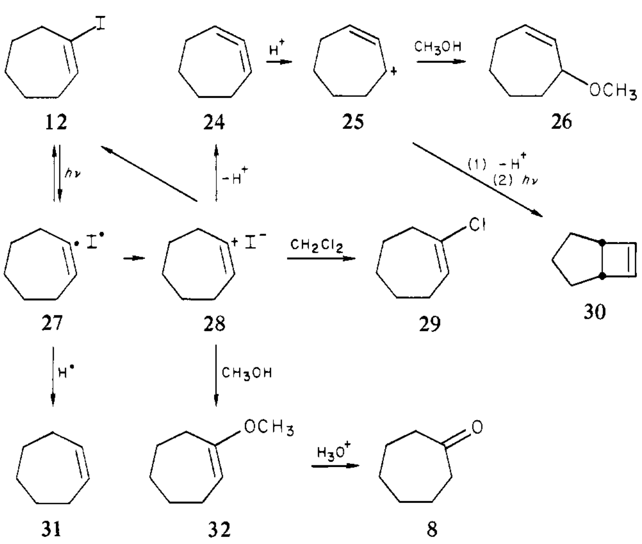


Table III. Irradiation of 1-Iodocycloheptene (**12**)[a]

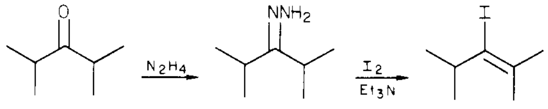
		yield,[b] %						
solvent	time, h	**12**	**26**	**29**	**30**	**31**	**32**	**8**
CH_3OH	10	*c*	13		2	31	11	26
CH_2Cl_2	10	*c*		44	18	7		

[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Trace.

Scheme IV

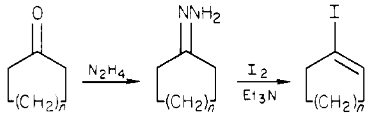


the general resistance of alkylvinyl halides toward ground-state solvolysis,[5] iodide **2** was recovered quantitatively from extended treatment with methanolic silver nitrate in the dark. By contrast, on irradiation in methanol at 254 nm it was rapidly converted to a mixture of the allylic ether **3**, the reduction product **5**, and the 1,3-diene **6** (Scheme II and Table I). On irradiation in dichloromethane or pentane the reduction product **5** and the 1,3-diene **6** were obtained. When the irradiation was conducted in methanol-*d*, the resulting allylic ether **3** was formed with 72% incorporation of deuterium at the vinylic position C-3, as determined by ^1H NMR analysis. Monitoring of the irradiation of **2** in methanol by gas chromatography revealed the presence of a peak corresponding in retention time to that of allene **4** but in low (<1%) yield. Irradiation under similar conditions of a methanolic solution of ethyl iodide containing 1 molar equiv of allene **4** resulted in the rapid formation of a mixture of the methyl ether **3** and the 1,3-diene **6**. Reaction continued on standing in the dark. The yield of diene **6** obtained from irradiation of iodide **2** in methanol decreased on extended irradiation. Another control experiment involving irradiation of a methanolic solution of ethyl iodide containing 1 molar equiv of diene **6** resulted in substantial loss of the diene accompanied by formation of ether **3** in low yield.



1 2

1-Halocycloalkenes. The homologous series of 1-iodocycloalkenes **11**–**14**[9,10] was prepared in a manner analogous to the preparation of iodide **2**. As shown in Scheme III and Table II, 1-iodocyclooctene (**11**) displayed photobehavior similar to that of iodide **2**. Thus irradiation of iodide **11** in methanol afforded principally the allylic ether **17**[11] and the reduction product **22**, in analogy with the formation of **3** and **5** from iodide **2**. Also formed were the nucleophilic trapping product **23**[12] and ketone **7**, which presumably arose by hydrolysis of the water-sensitive enol ether **23** during workup. Finally, the 1,3-diene **20** was obtained—along with the bicyclic alkene **21**,[13] to which **20** was found to undergo photocyclization. In dichloromethane the principal photoproducts from iodide **11** were the 1,3-diene **20** and its secondary photocyclization product **21**, accompanied by a small amount of the reduction product **22**.



7, $n = 3$
8, $n = 2$
9, $n = 1$
10, $n = 0$

11, $n = 3$
12, $n = 2$
13, $n = 1$
14, $n = 0$

As shown in Scheme IV and Table III, the next lower homologue, iodide **12**,[10] displayed qualitatively similar behavior.

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(10) Bottini, A. T.; Frost, K. A., II; Anderson, B. R.; Dev, V. *Tetrahedron* **1973**, *29*, 1975–1981.

(11) Seyferth, D.; Mai, V. A. *J. Am. Chem. Soc.* **1970**, *92*, 7412–7424.

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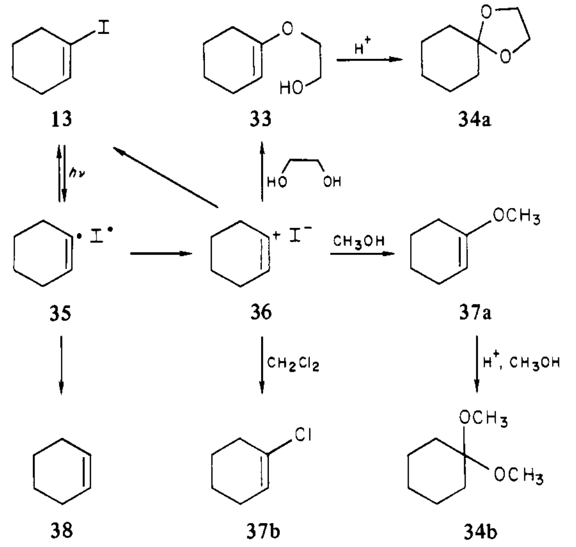
Table IV. Irradiation of 1-Iodocyclohexene (13)[a]

solvent	temp, °C	time, h	yield,[b] %				$\frac{34 + 37}{38}$
			13	34	37	38	
CH_3OH	40	10	*c*	72		26	2.8
CH_3OH[d]	40	10	*c*	8	65	27	2.7
CH_3OH	−25	5	37	55		8	6.9
$(CH_2OH)_2$	40	6	41	45		12	3.8
$(CH_2OH)_2$	−5	6	41	49		4	12.3
CH_2Cl_2	40	6	3		64	18	3.6
CH_2Cl_2	−20	6	16		66	5	13.2

[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Trace. [d] Zinc metal present; solution stirred during irradiation.

Scheme V



However, the allylic ether **26**[11] was obtained in lower yield than the corresponding product **17** from iodide **11**, as was the secondary photocyclization product **30**;[14] there was no detectable 1,3-diene present. By contrast, the nucleophilic trapping product in methanol, the enol ether **32**,[12] and its hydrolysis product **8** were obtained in substantially increased yields relative to the corresponding products **23** and **7** from iodide **11**. Moreover, in dichloromethane the nucleophilic trapping product **29**[15,16] was obtained as the principal product, whereas there was no detectable formation of the corresponding product from iodide **11**. Finally, there was no significant difference in the amount of the reduction products **22** and **31** formed from iodides **11** and **12**.

Reducing the ring size to six membered eliminated the formation of products derived from a 1,2-diene intermediate. Thus, as shown in Scheme V and Table IV, irradiation of 1-iodocyclohexene (**13**)[9] in methanol afforded principally the dimethyl ketal **34b**,[17] which was apparently a secondary product arising from acid-catalyzed addition of methanol to the nucleophilic trapping product **37a**.[12,18] In the presence of zinc metal as an acid scavenger the enol ether **37a** was obtained instead. Similarly, irradiation in ethane-1,2-diol or dichloromethane afforded principally the nucleophilic substitution products **34a**[19] or **37b**,[20] respectively.

Table V. Irradiation of 1-Iodocyclopentene (14)[a]

solvent	temp, °C	time, h	yield,[b] %			
			14	42	43	44
CH_3OH	40	6	18	76	*c*	*c*
CH_3OH	−25	6	69	25	4	*c*
CH_2Cl_2	40	10	11	70	*c*	*c*
CH_2Cl_2	−25	6	39	41	*c*	11

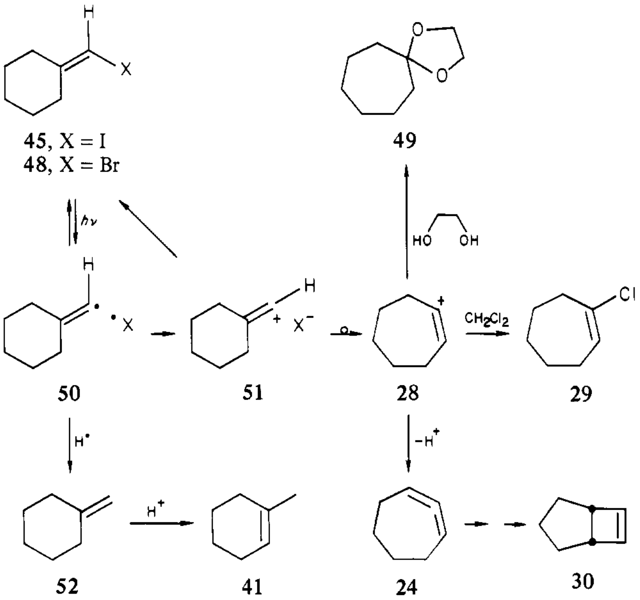
[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] None detected.

Table VI. Irradiation of (Halomethylene)cyclohexanes 45 and 48[a]

halide	solvent	temp, °C	time, h	yield,[b] %					
				halide	52	41	29	30	49
45	CH_2Cl_2	40	10	33	*c*	31	11	5	
45	CH_2Cl_2	−20	6	63	15	*c*	12	2	
45	$(CH_2OH)_2$	25	12	33	16	4			25
48[d]	$(CH_2OH)_2$	25	15	11	48	*c*			14

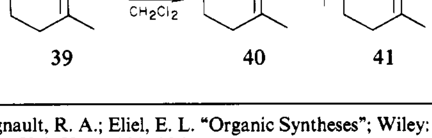
[a] Unless otherwise indicated, irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Trace. [d] Conducted using the broad emission of a 450-W Hanovia mercury arc.

Scheme VI



The photobehavior of iodide **13** was found to be somewhat sensitive to the temperature of the medium. Thus, as shown in Table IV, decreasing the temperature resulted in a modest increase in the ratio of the nucleophilic trapping products **34** and **37** to the reduction product **38**.

By contrast the 2-methyl derivative **39**[21] displayed more complex photobehavior, affording the nucleophilic substitution product **40**[21] and the reduction product **41** in substantially lower yields (21 and 12%, respectively) than the corresponding products from 1-iodocyclohexene (**13**). A complex mixture of unidentified hydrocarbon products was also obtained.



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(14) (a) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *12*, 186–189. (b) Chapman, O. L.; Pasto, D. J.; Borden, G. W.; Griswold, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 1220–1224.

(15) Ball, W. J.; Lander, S. R. *J. Chem. Soc.* **1962**, 2298–2304.

(16) Nucleophilic trapping by dichloromethane is precedented. See: Johnson, W. S.; Gravestock, M. B.; Parry, R. J.; Okorie, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 8604–8605. White, E. H.; McGirk, R. H.; Aufdermarsh, C. A., Jr.; Tiwari, H. P.; Todd, M. J. *Ibid.* **1973**, 95, 8107–8113. By contrast, radical abstraction occurs at hydrogen. See: Scherer, K. V., Jr.; Lunt, R. S., III *J. Am. Chem. Soc.* **1966**, *88*, 2860–2862.

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(20) Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2014–2019.

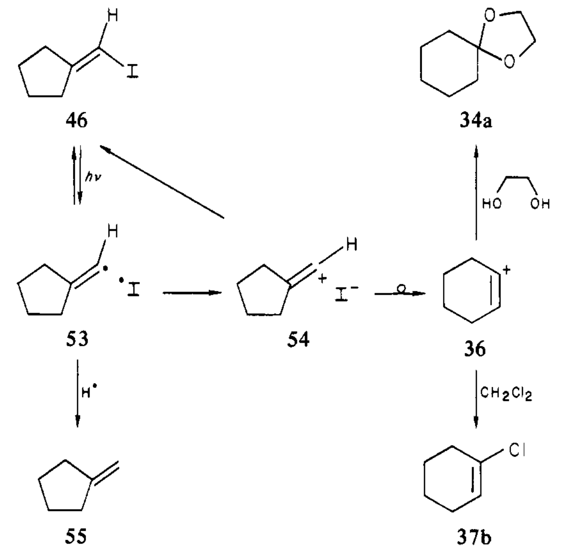
(21) Bottini, A. T.; Carson, F. P.; Fitzgerald, R.; Frost, K. A., II *Tetrahedron* **1973**, *28*, 4883–4902. For a recent description of the complex mixture of products obtained on solvolysis of the corresponding triflate, see: Hanack, M.; Fuchs, K.-A.; Collins, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 4008–4017.

Table VII. Irradiation of (Iodomethylene)cyclopentane (46)[a]

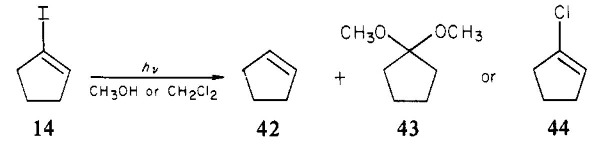
solvent	time, h	yield,[b] % 46	55	34a	37b
CH_2Cl_2	10	26	22		14
$(CH_2OH)_2$	10	36	32	23	

[a] Irradiations were conducted at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture.

Scheme VII



Finally, the cyclopentenyl homologue **14** displayed a notable reluctance to afford ionic photoproducts. As seen in Table V, irradiation of iodide **14** in methanol or dichloromethane at 40 °C afforded the reduction product cyclopentene (**42**) in high yield with no detectable formation of the ionic products **43**[22] or **44**.[23] However, lowering the temperature to −25 °C resulted in the formation of these products in moderate yields.



(Halomethylene)cycloalkanes. The exocyclic analogues **45**–**47**[24,25] were prepared by treating the hydrazones of the corresponding aldehydes with iodide and triethylamine as described above; however, it was found necessary to treat the resulting product with potassium *tert*-butoxide to effect complete dehydroiodination of the geminal diiodide intermediate. As shown in Scheme VI and Table VI, irradiation of (iodomethylene)cyclohexane (**45**)[24] in ethane-1,2-diol afforded the ring-expanded ketal **49**,[26] along with the reduction product methylenecyclohexane (**52**) and its acid-catalyzed rearrangement product 1-methylcyclohexene (**41**). In dichloromethane these latter products were accompanied by the rearranged vinyl chloride **29** and bicyclo[3.2.0]hept-6-ene (**30**). As discussed above, this product presumably arises via secondary photocyclization of 1,3-cycloheptadiene formed via deprotonation of the rearranged 1-cycloheptenyl cation (**28**). The corresponding bromide **48**[27] afforded principally the reduction product **52** in ethane-1,2-diol, along with some of the ketal **49**.

Table VIII. Irradiation of (Iodomethylene)cyclobutane (47)[a]

temp, °C	time, h	yield,[b] % 47	60	56	44	61
40	6	2	2	2	6	60
−25	6	17	1	c	7	49

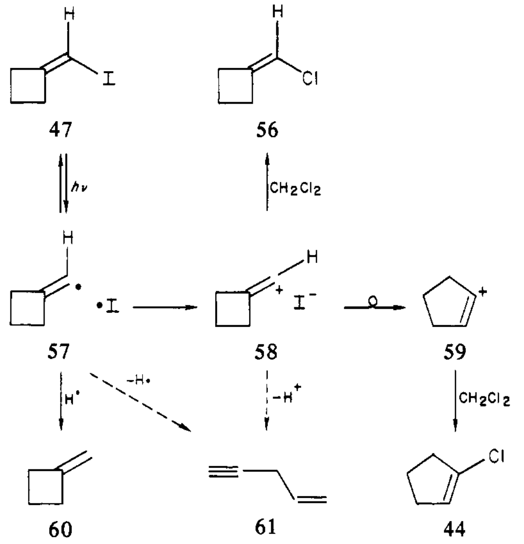
[a] Irradiations were conducted in dichloromethane solution at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Trace.

Table IX. Irradiation of the (Dihalomethylene)cyclohexanes 62–64[a]

dihalide	time, min	yield,[b] % dihalide	45/48/69	52	67/68
62	45	26	28		28
63	10	17	65		3
63[c]	20	7	49	6	11
64[c]	30	10	53	7	d

[a] Unless otherwise indicated, irradiations were conducted in methanol solution at 254 nm as described in the Experimental Section. [b] Determined by gas-chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the irradiation mixture. [c] Conducted with use of the broad emission of a 450-W Hanovia mercury arc. [d] None detected.

Scheme VIII



Similar behavior was exhibited by the cyclopentyl analogue **46**, which afforded the ring-expanded ketal **34a** in ethane-1,2-diol and the chloride **37b** in dichloromethane, accompanied by substantial amounts of the reduction product methylenecyclopentane (**55**). In this case there were no detectable products from deprotonation of the smaller 1-cyclohexenyl cation (**36**).

The cyclobutyl homologue **47** afforded only a small amount of the cyclopentenyl derivative **44**[23] in dichloromethane, accompanied by some of the unrearranged chloride **56**[25] and the reduction product **60**. The principal product was the enyne **61**,[28] apparently formed by competing fragmentation of the unrearranged cation **58**. In this case there was no appreciable effect of lowering the temperature.

(Dihalomethylene)cyclohexanes. Comparison was made with the photobehavior of the geminal dihalide analogues **62**–**64**. Irradiation of the diiodide **62**[29] in methanol afforded the reduction product **45**[24] and the highly unstable nucleophilic trapping product **67**. No products from ring expansion were observed. By contrast, the dibromo analogue **63**[30] afforded principally the reduction product **48**,[27] accompanied by only small amounts of the nu-

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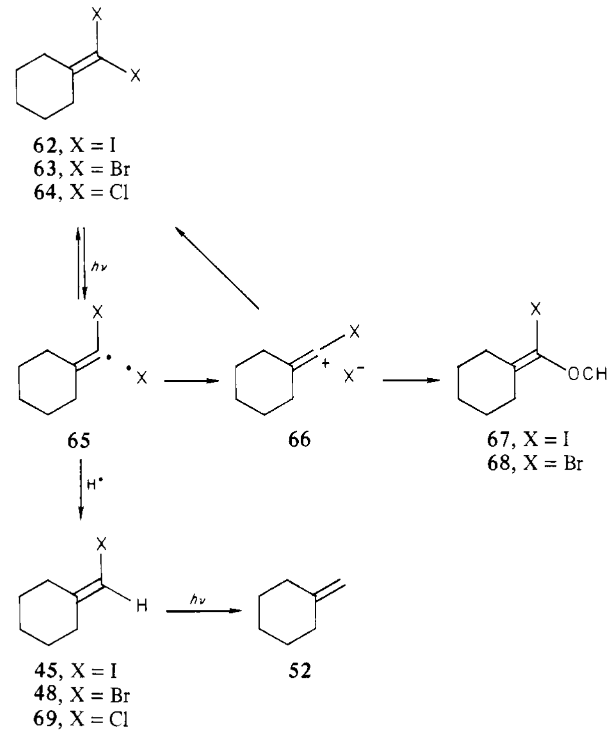
Scheme IX



cleophilic substitution product **68**. The dichloro analogue **64**[30,31] afforded only the reduction product **69**[32,33] and some of the further reduction product **52**, which presumably arises from secondary irradiation of the primary product **69**. There was no detectable formation of nucleophilic substitution product in this case.

Discussion

Cationic Intermediates. In prior photochemical studies alkyl-substituted vinyl iodides had been found to undergo competing cis ⇌ trans isomerization, elimination of HI, and formation of products derived from the corresponding vinyl radicals.[34-37] There were no reports of carbocationic intermediates. However, the occurrence of skeletal rearrangements and formation of nucleophilic substitution products observed in the present studies show quite clearly that carbocationic intermediates are involved.[38] Indeed, irradiation of vinyl iodides has proven to be a convenient and powerful method for the generation of vinyl cations, which can be effected even at low temperatures and in solvents of widely varying polarity. The photobehavior of vinyl iodides thus closely parallels that of their saturated alkyl analogues.[3]

The cationic intermediates presumably arise in a manner analogous to that of saturated alkyl systems, for which the mechanism outlined in Scheme I has been suggested.[3] Since the geometries of cyclic vinyl cations reflect the tendency of vinyl cations to adopt a linear arrangement at the positive carbon, the 1-cyclohexenyl and 1-cyclopentenyl cations are greatly destabilized relative to their acyclic analogues,[39] and their formation indicates once again the powerfulness of the photochemical method for generating carbocationic intermediates. The former cation can be generated solvolytically from cyclohexenyl precursors only at very slow rates,[40] and formation of the 1-cyclopentenyl homologue by irradiation of iodide **14** is apparently the first example of its formation from a cyclopentenyl precursor.[41]

The observed fate of the resulting carbocations was greatly dependent on their structures. The cation from the acyclic iodide **2** apparently underwent deprotonation to allene **4**, which in the acidic medium was further converted to ether **3** and/or the 1,3-diene **6**, as outlined in Scheme II.[42,43] This conclusion is supported by the control study in which allene **4** was converted to a mixture of **3** and **6** when present as a methanolic solution of ethyl iodide was irradiated under similar conditions. The reaction is apparently acid catalyzed since it continued in the dark. This mechanism is further supported by the finding that ether **3** was formed with substantial incorporation of deuterium at C-3 when the irradiation was conducted in methanol-*d*. This precludes the alternative possibility that the allylic cation intermediate arises via a simple 1,2-hydride shift. The control study with diene **6** showed that acid-catalyzed addition of methanol to this product is a minor competing route to ether **3**. The formation of the elimination product **4** is consistent with our previous observation that the cationic intermediates obtained on irradiation of alkyl halides undergo predominant deprotonation rather than nucleophilic trapping in alcoholic media unless deprotonation is structurally inhibited.[3]

The observed behavior of the cationic intermediates derived from the 1-iodocycloalkenes **11**–**14** varied with ring size. The intermediate **19** from the cyclooctenyl homologue **11** underwent competing nucleophilic trapping and deprotonation in methanol but only deprotonation in the less nucleophilic solvent dichloromethane. In the next smaller cycloheptenyl system competing nucleophilic trapping and deprotonation were observed in both solvents. In this case the 1,2-diene **24** resulting from deprotonation is apparently sufficiently strained that nucleophilic trapping by dichloromethane can compete with deprotonation.[16] Finally, in the cyclohexenyl and cyclopentenyl systems only nucleophilic trapping was observed. The 1,2-dienes that would result from deprotonation in these cases are apparently prohibitively strained for their formation to compete with nucleophilic trapping.[44]

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(37) Wilson, R. M.; Commons, T. J. *J. Org. Chem.* **1975**, *40*, 2891–2897.

(38) Cationic photochemical intermediates have also been recently observed from a number of aryl-substituted vinyl halides. See: (a) Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180. (b) Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752–756. (c) Suzuki, T.; Kitamura, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 5324–5328. (d) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Ibid.* **1982**, *47*, 2323–2328.

(39) See: Mayr, H.; Schneider, R.; Wilhelm, D.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 5336–5340.

(40) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513–1516. Subramanian, L. R.; Hanack, M. *Chem. Ber.* **1972**, *105*, 1465–1470.

(41) Although solvolysis of 1-cyclopentenyl triflate and nonaflate has been reported,[40] reaction in these cases apparently involves nucleophilic attack at sulfur rather than ionization to the cyclopentenyl cation. See: Hanack, M.; Bentz, H.; Märkl, R.; Subramanian, L. R. *Liebigs Ann. Chem.* **1978**, 1894–1904.

(42) It has been suggested previously that elimination photoproducts from alkyl iodides arise via disproportionation of the initially formed caged radical pair.[36] This seems unlikely since alkyl bromides typically afford little or no elimination product[1,3] and yet bromine atoms are substantially more reactive toward hydrogen atom abstraction than iodine. The proposed intermediacy of a carbocation in the elimination process is also more consistent with the competition between elimination and nucleophilic substitution observed for the cycloalkenyl series **11**–**13**.

(43) Allenes normally undergo protonation at the central carbon atom to afford allylic cations. See: Stang, P. J. *Prog. Phys. Org. Chem.* **1973**, *10*, 205–325. Note also: Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317–359.

(44) (a) It is assumed that the allylic ether **17** and 1,3-cyclooctadiene (**20**) from 1-iodocyclooctene (**11**) and the corresponding allylic ether **26** and 1,3-cycloheptadiene from 1-iodocycloheptene (**12**) arise via mechanisms analogous to that demonstrated for the acyclic system **2** (Scheme II), although this question was not explicitly studied. 1,2-Cyclooctadiene (**15**) has not been isolated but can be maintained for short times in cold solution. See: Marquis, E. T.; Gardner, P. D. *Tetrahedron Lett.* **1966**, 2793. 1,2-Cycloheptadiene has previously been proposed as a reactive intermediate. See: Wittig, G.; Meske-Schüller, J. *Justus Liebigs Ann. Chem.* **1968**, *711*, 76. Ball, W. J.; Landor, S. R. *J. Chem. Soc.* **1962**, 2298. (b) It is conceivable that nucleophilic substitution products obtained from irradiation of the cycloheptenyl and cyclohexenyl iodides **12** and **13** in methanol or ethane-1,2-diol arise in part via initial light-induced cis ⇌ trans isomerization followed by protonation of the resulting highly strained *trans*-cycloalkene. See: Kropp, P. *J. Org. Photochem.* **1979**, *4*, 1–142.

The cations generated on irradiation of the (iodomethylene)cycloalkanes **45** and **46** have the interesting dilemma of either being α-unsubstituted, as formed, or undergoing rearrangement to the 1-cycloalkenyl cation **28** or **36**, in which case they then bear a stabilizing α substituent but can no longer assume the preferred linear geometry. The observation of only products from trapping of the rearranged cation **28** or **36** indicates that the latter is preferred.[45,46] As expected from involvement of the 1-cycloheptenyl cation **28** on irradiation of either iodide **12** or iodide **45**, chloride **29** and the secondary photocyclization product **30** were obtained in approximately the same ratio (2.3–2.4:1) on irradiation of either iodide.

The smaller homologue (iodomethylene)cyclobutane (**47**) proved to be a poor precursor to the highly strained 1-cyclopentenyl cation. In addition to the formation of small amounts of the ring-expanded product **44**, some direct trapping of the unrearranged cation occurred to give chloride **56**. The principal course of reaction, however, was fragmentation to the enyne **61**, which afforded a relief of strain of the cyclobutyl system. It is not clear whether the cation **58** or the initially formed radical **57** is involved in the fragmentation to **61**.

(Dihalomethylene)cyclohexanes. The geminal dihalides **62–64** underwent selective cleavage of a single carbon–halogen bond to afford products emanating from the resulting α-halo radical or α-halo cation. There was no apparent formation of products from the corresponding vinylcarbene intermediate. This behavior parallels that of the corresponding saturated analogues.[1]

Iodides vs. Bromides and Chlorides. The bromides **48** and **63** afforded substantially lower ratios of ionic to radical products than the corresponding iodides **45** and **62**. The dichloride **64** afforded only radical-derived products. This trend parallels that observed previously in saturated geminal dihalides and monhalides, but its origin is not clear.[1,3] It might be expected that the more electronegative bromine or chlorine atom would undergo electron transfer more readily than iodine. There are, however, several possible offsetting effects. Bromine and chlorine 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. Also, the greater polarizability of iodine might facilitate electron transfer. Finally, formation of the larger iodide ion involves generation of a lower charge density.

Temperature Effect. Lowering the temperature of the irradiation of iodides **13**, **14**, and **45** resulted in an increase in the ratio of ionic to radical products. The origin of this effect is not clear. It was previously shown that with saturated alkyl iodides and bromides solvents of higher viscosity also afforded increased ratios of ionic to radical products,[3] a phenomenon also exhibited by iodide **13** on going from methanol to ethane-1,2-diol. However, the temperature effect is apparently not attributable simply to an increase in the solvent viscosity because saturated alkyl halides do not exhibit a similar temperature effect.[47] It is not clear why the effect is exhibited by vinyl but not saturated systems. Nonetheless, lowering the temperature is a highly useful technique, along with increasing the solvent viscosity, for enhancing the production of carbocationic intermediates in vinyl systems.

We continue to explore the varied and synthetically useful solution photobehavior of alkyl halides.

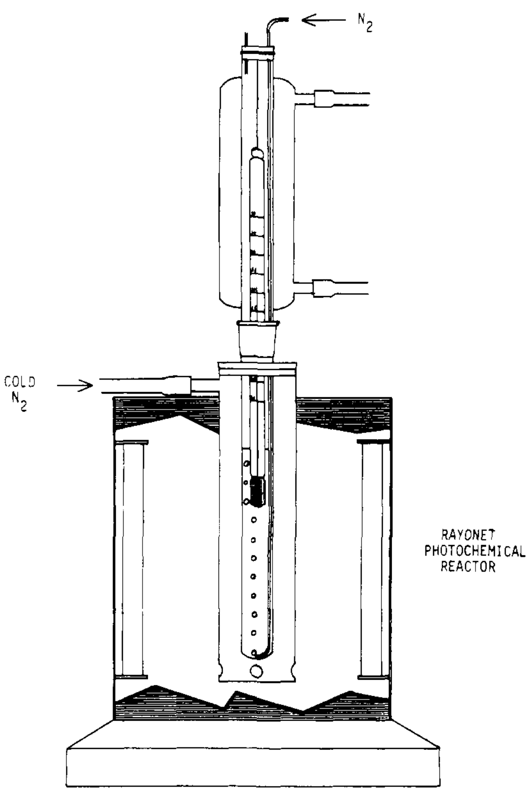

Figure 1. Low-temperature photolysis apparatus.

Experimental Section

General Procedures. Gas-chromatographic analyses were performed on a Hewlett-Packard 5750 or a Varian Aerograph 90-P instrument using either 10-ft × 0.125-in. stainless steel columns containing 20% SF-96 or 20% Carbowax 20M on 60–80 mesh Chromosorb W or a 22-ft × 0.25-in. stainless steel column containing 20% β,β-oxydipropionitrile on 60–80 mesh Chromosorb P. Melting points were determined by using a Thomas-Hoover capillary apparatus and are uncorrected and uncalibrated. Infrared spectra were obtained either neat or in carbon tetrachloride solution with a Perkin-Elmer 421 grating spectrophotometer; ultraviolet spectra were obtained in absolute ethanol with a Cary 14 spectrophotometer. Proton NMR spectra were determined in either carbon tetrachloride or chloroform-*d* solution with a Jeolco C-60HL spectrometer or a Varian XL-100 spectrometer; data are reported in the following manner: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = heptet, m = unresolved multiplet, and br = broadened); integration; coupling constant; and assignment when possible. Mass spectra were obtained by 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. A 10-mL 0.05 M solution of the iodide containing an internal hydrocarbon standard was placed in a quartz tube (200 × 9 mm) equipped with a condenser and a nitrogen inlet tube and suspended either in a Rayonet RPR-100 photochemical reactor fitted with a circular array of 16 G8T5 (254-nm) lamps or 4 cm in front of a Hanovia 450-W mercury lamp mounted in a reflector. In the latter case cooling was effected by a stream of air across the tube. Unless otherwise indicated, the solution was purged with nitrogen for 10 min prior to irradiation and maintained under a nitrogen atmosphere. Low-temperature irradiations were conducted by using the apparatus depicted in Figure 1. The flow of cold nitrogen, and hence the temperature of the irradiation solution, was controlled by varying the current passing through a heating coil located inside a Dewar flask containing liquid nitrogen.

At the completion of the irradiation the usually yellow solution was poured into 80 mL of 5% aqueous sodium bicarbonate solution and extracted with two 10-mL portions of pentane or ether. The combined organic layers were washed with a 5-mL portion of 10% sodium thiosulfate solution followed by a 20-mL portion of saturated sodium chloride solution, dried over anhydrous granular sodium sulfate, filtered, and concentrated by distillation of the solvent through a Vigreux column. Products were isolated by preparative gas chromatography.

2,4-Dimethyl-3-iodo-2-pentene (2). A. Preparation. Iodide **2** was

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(45) By contrast, radical analogues of cation **51** do not undergo ring expansion. See: Julia, M. *Rec. Chem. Prog.* **1964**, *25*, 3–29.

(46) α-Unsubstituted vinyl cations have previously been proposed as possible intermediates in the decomposition of diazonium ions generated in alkaline media. See: Newman, M. S.; Kutner, A. *J. Am. Chem. Soc.* **1951**, *73*, 4199–4204. Newman, M. S.; Weinberg, A. E. *Ibid.* **1956**, *78*, 4654–4655. Newman, M. S.; Beard, C. D. *Ibid.* **1970**, *92*, 7564–7567. However, in some cases carbene intermediates appear to be involved. See: Curtin, D. Y.; Kampmeier, J. A.; O'Connor, B. R. *Ibid.* **1965**, *87*, 863–873. Of particular interest is the report that treatment of the corresponding *N*-nitrosooxazolidones with base in the presence of lithium iodide afforded iodides **45** and **46** in high yield via a proposed trapping of vinyl cations **51** and **54**, respectively, by iodide ion.[24] No rearrangement to the ring-expanded cations **28** and **36** was observed. This suggests either that vinyl cations are not involved in the base-initiated reactions or that the vinyl cations **51** and **54** have different behavior dependent on their mode of formation.

(47) McNeely, S. A. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1976.

prepared by using a modification of the general procedure of Pross and Sternhell.[9] Into a 2-necked 100-mL round-bottomed flask equipped with a magnetic stirring bar, condenser, and addition funnel was placed 30.0 g (600 mmol) of hydrazine hydrate. A solution of 10.0 g (87.0 mmol) of 2,4-dimethyl-3-pentanone (**1**) in 25 mL of absolute ethanol was added very slowly (less than 5 drops per min) to the hydrazine hydrate with vigorous stirring. After the addition was complete, the contents of the flask were heated to reflux for 1 h and then cooled to room temperature, after which most of the ethanol was removed under aspirator pressure. The reaction mixture was then extracted with two 100-mL portions of chloroform. The combined chloroform layers were washed successively with two 50-mL portions of saturated sodium chloride solution and dried over anhydrous sodium sulfate. After filtration, the chloroform was removed by distillation through a Vigreux column to yield 11.5 g of greenish oil, which upon distillation at 90–91 °C (43 mm) afforded 9.6 g (74 mmol, 85%) of hydrazone.

A solution of 8.5 g (67 mmol) of this hydrazone in 100 mL of dry triethylamine was placed into a 200-mL round-bottomed flask equipped with an addition funnel, magnetic stirring bar, and calcium sulfate drying tube. The flask was cooled to 0 °C in an ice bath and a saturated solution of iodine in tetrahydrofuran, which had been distilled with lithium aluminum hydride, was added rapidly via the addition funnel to the hydrazone solution with vigorous stirring until the evolution of nitrogen ceased and the color of the reaction mixture changed from light yellow to brown. The reaction mixture was stirred at room temperature for 1 h and then poured into 400 mL of ice water. The aqueous layer was extracted with three 100-mL portions of pentane, and the combined pentane layers were washed with four 100-mL portions of cold 1 N hydrochloric acid. During the fourth wash, the color of the pentane layer turned from yellow to dark orange. The pentane layer was then washed with one 50-mL portion each of saturated sodium bicarbonate and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and filtered. Removal of the pentane under reduced pressure yielded 8.5 g of a pink oil, which on distillation at 44–45 °C (2 mm) afforded 7.50 g (33.5 mmol, 54%) of iodide **2** as a colorless oil: λ_{max} 256 nm (ϵ 340); ν_{max} (CCl_4) 2963, 2925, 2866, 1623, 1452, 1380, 1361, 1307, 1209, 1100, 950, 851, 817 cm^{-1}; ^{1}H NMR (CCl_4) τ 7.67 (h, 1, *J* = 6.2 Hz, CH-4), 8.1 and 8.15 (2 s, 6, $=C(CH_3)_2$), 9.1 (d, 6, *J* = 6.2 Hz, $(CH_3)_2C$); lit.[8] ^{1}H NMR (CCl_4) τ 7.63 (m, 1), 8.08 and 8.14 (2 s, 6), 9.07 (d, 6, *J* = 6.5 Hz).

B. Treatment with Methanolic Silver Nitrate. A 0.05 M methanolic solution of iodide **2** containing 2 molar equiv of silver nitrate and a hydrocarbon standard was maintained at 41 °C for 10 h. Gas-chromatographic analysis revealed no loss in the amount of iodide and no detectable formation of any products.

C. Irradiation. From the irradiations described in Table I, the following products were isolated.

2,4-Dimethyl-4-methoxy-2-pentene (**3**) was obtained as a colorless liquid: ν_{max} (CCl_4) 2973, 2933, 2826, 1666, 1445, 1381, 1361, 1248, 1171, 1131, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 4.92 (m, 1, CH-3), 6.84 (s, 3, $-OCH_3$), 8.1 and 8.15 (2 d, 6, *J* = 1.2 and 1.5 Hz, $=C(CH_3)_2$), 8.70 (s, 6, $(CH_3)_2C$-4); *m/e* 128.1202 (calcd for $C_8H_{16}O$, 128.1201), 128 (4), 113 (100), 107 (16), 106 (33), 81 (52), 79 (23).

2,4-Dimethyl-2-pentene (**5**) was obtained as a colorless liquid that had an infrared spectrum and a gas-chromatographic retention time identical with those of a commercial sample.

2,4-Dimethyl-1,3-pentadiene (**6**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3091, 2976, 2936, 2920, 2865, 1650, 1626, 1449, 1376, 1069, 891 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 4.22 (m, 1, CH-3), 5.12 and 5.33 (2 m, 2, CH_2-1), 8.23 (m, 9, CH_3C-2 and $=C(CH_3)_2$); lit.[48] ν_{max} (CCl_4) 3090, 1650, 890 cm^{-1}.

1-Iodocyclooctene (11). A. Preparation. Treatment of 5.3 g (40 mmol) of the hydrazone of cyclooctanone (**7**) in 75 mL of triethylamine according to the modification of the general procedure of Pross and Sternhell[9] described above gave 8.3 g of a dark red oil. Distillation at 41–41.5 °C (0.3 mm) afforded 5.1 g (23 mmol, 59% based on cyclooctanone) of iodide **11** as a colorless oil: λ_{max} 259 nm (ϵ 380); ν_{max} (CCl_4) 3035, 2930, 2858, 1627, 1461, 1446, 1210, 1109 cm^{-1}; ^{1}H NMR (CCl_4) τ 3.77 (t, 1, *J* = 8.1 Hz, CH-2), 7.37 (m, 2, CH_2-8), 7.94 (m, 2, CH_2-3), 8.50 (m, 8, 4 × CH_2); *m/e* 236.0067 (calcd for $C_8H_{13}I$, 236.0064), 236 (27), 128 (4), 127 (6), 108 (44), 81 (19), 79 (20), 67 (100).

B. Irradiation. From the irradiations outlined in Table II the following products were isolated.

Cyclooctanone (**7**), **1,3-cyclooctadiene** (**20**), and **cyclooctene** (**22**) were obtained as colorless materials that were identical with commercial specimens. *cis*-Bicyclo[4.2.0]oct-7-ene (**21**) was obtained as a colorless liquid having an infrared spectrum in agreement with that previously published.[13]

3-Methoxycyclooctene (**17**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3061, 3021, 2982, 2930, 2861, 2821, 1656, 1450, 1188, 1142, 1130, 1097, 943, 710 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.60 (m, 2, CH-1 and -2), 6.10 (m, 1, CH-3), 6.85 (s, 3, $-OCH_3$), 8.5 (m, 10, 5 × CH_2); lit.[11] ν_{max} (CCl_4) 1650 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.1–4.75 (m, 2), 5.8–6.2 (m, 1), 6.8 (s, 3), 7.6–8.95 (m, 10).

1-Methoxycyclooctene (**23**) was obtained as a colorless oil: ν_{max} (CCl_4) 3067, 3001, 2927, 2857, 2833, 1659, 1462, 1450, 1379, 1263, 1252, 1232, 1200, 1156, 1104, 1094, 1032 cm^{-1}; ^{1}H NMR (CCl_4) τ 5.70 (t, 1, *J* = 8.2 Hz, CH-2), 6.63 (s, 3, $-OCH_3$), 7.90 (m, 4, CH_2-3 and -8), 8.55 (m, 8, 4 × CH_2); lit.[12] ν_{max} (CCl_4) 1667; ^{1}H NMR (CCl_4) τ 5.63, 6.60.

Irradiation of 1,3-Cyclooctadiene (20). A solution containing 50 mg of diene **20** in 10 mL of dichloromethane was irradiated at 254 nm as described above. Gas-chromatographic analysis revealed the formation of the cyclobutene **21** in 36% yield and a 62% recovery of diene **20**. Isolation by preparative gas chromatography afforded cyclobutene **21** as a colorless liquid identical with that obtained from iodide **11** as described above.

1-Iodocycloheptene (12). A. Preparation. Treatment of 11.3 g (90 mmol) of the hydrazone of cycloheptanone (**8**) as described above gave 15.6 g of a red oil, which on distillation at 80–82 °C (7 mm) afforded 9.6 g (43 mmol, 48% based on cycloheptanone) of iodide **12** as a colorless oil: λ_{max} 263 nm (ϵ 351); ν_{max} (CCl_4) 3042, 2929, 2856, 1627, 1443, 948, 892, 843 cm^{-1}; ^{1}H NMR (CCl_4) τ 3.65 (t, 1, *J* = 6.0 Hz, CH-2), 7.27 (m, 2, CH-7), 7.94 (m, 2, CH_2-3), 8.35 (m, 6, 3 × CH_2); lit.[10] bp 79–80 °C (7 mm); ν_{max} (CCl_4) 1625 cm^{-1}; ^{1}H NMR (CCl_4) τ 3.55 (t, 1), 7.25 (m, 2), 7.9 (m, 2), 8.35 (m, 6).

B. Irradiation. From the irradiations outlined in Table III the following photoproducts were isolated.

Cycloheptanone (**8**) and **cycloheptene** (**31**) were obtained as colorless liquids that were identical with commercial specimens.

3-Methoxycycloheptene (**26**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3031, 2983, 2931, 2860, 2822, 1642, 1443, 1107, 1099, 977, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 4.2 (m, 2, CH-1 and -2), 6.15 (m, 1, CH-3), 6.64 (s, 3, $-OCH_3$), 8.5 (m, 8, 4 × CH_2); lit.[11] ν_{max} (CCl_4) 1650 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.35 (m, 2), 6.3 (m, 1), 6.8 (m, 3), 7.8–9.0 (m, 8).

1-Chlorocycloheptene (**29**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3050, 2932, 2863, 1644, 1445, 1353, 1039, 965, 921, 844 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.30 (t, 1, *J* = 6.5 Hz, CH-2), 7.53 (m, 2, CH-7), 7.60 (m, 2, CH_2-3), 8.33 (m, 6, 3 × CH_2); lit.[15] ν_{max} 1660 cm^{-1}.

Bicyclo[3.2.0]hept-6-ene (**30**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3121, 3040, 2941, 2852, 1661, 1443, 1322, 1298, 1258, 1052, 931, 892, 842 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.17 (s, 2, CH-6 and -7), 6.85 (d, 2, *J* = 6.1 Hz, CH-1 and -5), 8.50 (m, 6, 3 × CH_2); lit. ν_{max} 3020, 1660, 735 cm^{-1};[14a] ^{1}H NMR (CCl_4) τ 4.24 (s, 2), 6.89 (d, 2, *J* = 6.0 Hz), 8.58 (m, 6).[14b]

1-Methoxycycloheptene (**32**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3071, 3000, 2923, 2852, 1666, 1443, 1379, 1280, 1231, 1192, 1169, 1124, 1109, 1041, 997, 963, 943 cm^{-1}; ^{1}H NMR (CCl_4) τ 5.47 (t, 1, *J* = 6.0 Hz, CH_2-2), 6.66 (s, 3, $-OCH_3$), 7.84 (m, 4, CH_2-3 and -7), 8.41 (m, 6, CH_2-4, -5, and -6); lit.[12] ν_{max} (CCl_4) 1657; ^{1}H NMR (CCl_4) τ 5.40, 6.63.

Irradiation of 1-Iodocyclohexene (13).[9] From the irradiations outlined in Table IV the following products were isolated.

1,4-Dioxaspiro[4.5]decane (**34a**) was obtained as a colorless liquid identical with a specimen prepared as described previously:[19] ν_{max} (CCl_4) 2937, 2866, 1444, 1362, 1279, 1157, 1096, 1034, 920 cm^{-1}; ^{1}H NMR (CCl_4) τ 6.23 (s, 4, CH_2-2 and -3), 8.51 (m, 10, 5 × CH_2); lit.[19] no spectral data.

1,1-Dimethoxycyclohexane (**34b**) was obtained as a colorless liquid identical with a specimen prepared independently: ν_{max} (CCl_4) 2943, 2865, 2844, 1463, 1450, 1365, 1275, 1255, 1183, 1159, 1104, 1075, 1054, 923, 909, 847 cm^{-1}; ^{1}H NMR (CCl_4) τ 6.97 (s, 6, $-OCH_3$), 8.53 (m, 10, 5 × CH_2); lit.[17] no spectral data.

1-Methoxycyclohexene (**37a**) was obtained as a colorless liquid: ν_{max} (CCl_4) 3063, 2999, 2931, 2842, 1664, 1447, 1378, 1339, 1268, 1209, 1179, 1159, 1029, 954 cm^{-1}; ^{1}H NMR (CCl_4) τ 5.4 (m, 1, CH-2), 6.55 (s, 3, $-OCH_3$), 8.0 (m, 4, CH_2-3 and -6), 8.40 (m, 4, CH_2-4 and -5); lit.[12,18] ν_{max} (CCl_4) 1670; ^{1}H NMR (CCl_4) τ 5.50 (m, 1), 6.61 (s, 3), 8.00 (m, 4), 8.40 (m, 4).

1-Chlorocyclohexene (**37b**) was obtained as a colorless liquid: λ_{max} 200 nm (ϵ 4370); ν_{max} (neat) 3047, 2935, 2864, 2843, 1657, 1447, 1437, 1355, 1263, 1138, 1047, 1005, 945, 914, 841, 830, 798, 728 cm^{-1}; ^{1}H NMR (CCl_4) τ 4.13 (m, 1, CH_2-2), 7.73 (m, 4, CH_2-3 and -6), 8.25 (m, 4, CH_2-4 and -5); lit.[20] no spectral data.

Cyclohexene (**38**) was obtained as a colorless liquid identical with a commercial specimen.

Irradiation of 1-Iodo-2-methylcyclohexene (**39**). A 0.05 M solution of iodide **39**[21] in dichloromethane was irradiated at 254 nm as described

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(48) *API Infrared Spectral Data* **1975**, 2960.

above for 8 h. Workup and isolation in the usual way afforded the following photoproducts.

1-Chloro-2-methylcyclohexene (40) was obtained as a colorless liquid: ν_{max} (CCl_4) 2931, 2882, 2857, 2840, 2831, 1673, 1448, 1438, 1377, 1335, 1015, 988, 924 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (m, 2, CH_2-6), 2.0 (m, 2, CH_2-3), 1.7 (m, 7, $-CH_3$ and 2 × CH_2); lit.[21] no spectral data.

1-Methylcyclohexene (41) was obtained as a colorless liquid identical with a commercial specimen.

Irradiation of 1-Iodocyclopentene (10).[9] From the irradiations described in Table V the following products were isolated.

Cyclopentene (42) was obtained as a colorless liquid identical with a commercial specimen.

1,1-Dimethoxycyclopentane (43) was obtained as a colorless liquid identical with a specimen prepared independently as described previously:[17] ν_{max} (CCl_4) 2956, 2839, 1644, 1451, 1332, 1189, 1112, 1049, 971 cm^{-1}; ^1H NMR (CCl_4) τ 6.90 (s, 6, 2 × $-OCH_3$), 8.36 (m, 8, 4 × CH_2); lit.[22] no data given.

1-Chlorocyclopentene (44) was obtained as a colorless liquid: λ_{max} 200 nm (ϵ 4620); ν_{max} (CCl_4) 3080, 2965, 2863, 1626, 1445, 1324, 1298, 1205, 1059, 947, 820 cm^{-1}; ^1H NMR (CCl_4) τ 4.53 (m, 1, CH-2), 7.75 (m, 6, 3 × CH_2); lit.[23] ν_{max} (CCl_4) 1628, 810 cm^{-1}; ^1H NMR (CCl_4) τ 4.45 (m), 7.25–8.34 (m).

(Iodomethylene)cyclohexane (45) and (Bromomethylene)cyclohexane (48). A. Preparation. Treatment of 5.0 g of the hydrazone of cyclohexylmethanal as described above afforded 8.0 g of a red oil, which was added to 300 mL of anhydrous *tert*-butyl alcohol in which 10 g of potassium metal had been dissolved. The resulting mixture was heated under reflux for 12 h, cooled to room temperature, poured into 500 mL of ice water, and extracted with three 50-mL portions of pentane. The combined organic layers were washed with three 50-mL portions of pentane. The combined organic layers were washed with three 50-mL portions of water and one 50-mL portion of saturated sodium chloride solution. After being dried over anhydrous sodium sulfate, the solution was filtered and concentrated under reduced pressure to yield 5.6 g of a red oil. Distillation at 48–49 °C (0.2 mm) afforded 5.1 g (23 mmol, 56%) of iodide **45** as a colorless liquid: λ_{max} 251 nm (ϵ 421); ν_{max} (CCl_4) 3055, 2934, 2863, 1614, 1449, 1275, 1228, 1162, 1124, 985 cm^{-1}; ^1H NMR (CCl_4) τ 4.33 (m, 1, =CHI), 7.60 (m, 4, CH_2-2 and -6), 8.50 (m, 6, CH_2-3, -4, and -5); lit.[24] bp 45–47 °C (0.2 mm); ^1H NMR (CCl_4) τ 4.23 (m, 1), 7.72 (m, 4), 8.43 (m, 6).

Bromide **48** was prepared as described previously.[27]

B. Irradiation. From the irradiations described in Table VI the following products were isolated as colorless liquids by preparative gas chromatography. 1-Chlorocycloheptene (**29**) and bicyclo[3.2.0]hept-6-ene (**30**) were identified by comparison with the specimens described above. 1-Methylcyclohexene (**41**) and methylenecyclohexane (**52**) were identified by comparison with commercial specimens.

1,4-Dioxaspiro[4.6]undecane (49) was obtained as a colorless liquid: ν_{max} (CCl_4) 2930, 2865, 1447, 1368, 1209, 1120, 1091, 1032, 946, 872 cm^{-1}; ^1H NMR (CCl_4) τ 3.70 (s, 4, CH_2-2 and -3), 8.47 (m, 12, 6 × CH_2); lit.[26] bp 53 °C (4 mm).

(Iodomethylene)cyclopentane (46). A. Preparation. Treatment of 9.0 g of cyclopentylmethanal as described above afforded 8 g of a crude mixture of vinyl iodide and diiodide, which was added directly to a solution of 8.5 g of potassium in 200 mL of anhydrous *tert*-butyl alcohol. The mixture was stirred for 14 h at room temperature and then poured into 600 mL of ice water. The aqueous mixture was extracted with three 100-mL portions of pentane, and the combined organic layers were washed with one 50-mL portion of saturated sodium chloride solution and then dried over anhydrous sodium sulfate. The pentane and most of the residual *tert*-butyl alcohol were removed at aspirator pressure to yield 4.2 g of a red oil. Distillation at 65–67 °C (4 mm) afforded 3.60 g (17.5 mmol, 43% based on cyclopentylmethanal) of iodide **46** as a colorless liquid: λ_{max} 251 nm (ϵ 411); ν_{max} (CCl_4) 3061, 2960, 2871, 1627, 1422, 1304, 1261, 1240, 1218, 1130, 1093, 945 cm^{-1}; ^1H NMR (CCl_4) τ 4.21 (m, 1, =CHI), 7.75 (m, 4, CH_2-2 and -5), 8.23 (m, 4, CH_2-3 and -4); lit.[24] bp 83–85 °C (15 mm); ^1H NMR (CCl_4) τ 4.15 (m, 1), 7.72 (m, 4), 8.20 (m, 4).

B. Irradiation. From the irradiations described in Table VII the following products were isolated as colorless liquids by preparative gas chromatography. 1,4-Dioxaspiro[4.5]decane (**34a**) and 1-chlorocyclohexene (**37b**) were identified by direct comparison with the specimens described above. Methylenecyclopentane (**55**) was identified by comparison with a commercial specimen.

(Iodomethylene)cyclobutane (47). A. Preparation. Treatment of 8.1 g of the hydrazone of cyclobutylmethanal, prepared by Sarett oxidation[49] of cyclobutylmethanol,[50] with iodine in triethylamine followed by treatment with potassium *tert*-butoxide as described above afforded 2.1 g of a red oil. Distillation at 69–70 °C (20 mm) afforded 1.22 g (6.29 mmol, 18% based on cyclobutylmethanal) of iodide **47** as a colorless liquid: λ_{max} 248 nm (ϵ 419); ν_{max} (CCl_4) 3069, 2994, 2960, 2924, 1646, 1414, 1249, 1203, 1045, 1006, 952, 905, 704 cm^{-1}; ^1H NMR (CCl_4) τ 4.45 (m, 1, =CHI), 7.52 (m, 4, CH_2-2 and -4), 8.23 (m, 2, CH_2-3); lit.[25] bp 68–70 °C (20 mm); ν_{max} (neat) 3090, 1655, 1255, 1210, 1050, 795, 704 cm^{-1}; ^1H NMR (CCl_4) τ 4.36 (m, 1), 7.42 (m, 4), 8.03 (m, 2).

B. Irradiation. From the irradiations described in Table VIII the following products were isolated as colorless liquids by preparative gas chromatography. 1-Chlorocyclopentene (**44**) was identified by comparison with the specimen described above and methylenecyclobutane (**60**) by comparison with a commercial sample.

(Chloromethylene)cyclobutane (56): ν_{max} (CCl_4) 3080, 2994, 2963, 2930, 1670, 1426, 1279, 1218, 955 cm^{-1}; ^1H NMR ($CDCl_3$) τ 4.28 (p, 1, J = 2.4 Hz, =CHCl), 7.25 (m, 4, CH_2-2 and -4), 8.0 (m, 2, CH_2-3); lit.[25] ν_{max} (neat) 2995, 2940, 1670, 1420, 1281, 960, 870, 720, 670 cm^{-1}; ^1H NMR ($CDCl_3$) τ 4.25 (m, 1), 7.25 (m, 4), 8.0 (m, 2).

1-Penten-4-yne (61): ν_{max} (CCl_4) 3320, 3096, 2992, 2901, 2130, 1643, 1420, 988, 918 cm^{-1}; ^1H NMR ($CDCl_3$) τ 4.20 (m, 1, CH-2), 4.75 (m, 2, CH_2-1), 7.02 (m, 2, CH_2-3), 7.89 (t, 1, J = 2.6 Hz, CH-5); lit.[28] ν_{max} (CCl_4) 3300, 2120, 990, 920 cm^{-1}.

Irradiation of (Diiodomethylene)cyclohexane (62). From the irradiation of diiodide **62**[29] described in Table IX the following products were isolated by preparative gas chromatography.

Iodide **45**[24] was obtained as a colorless liquid which was identified by direct comparison with the material described above.

(Iodomethoxymethylene)cyclohexane (67) was obtained as an unstable colorless liquid which rapidly blackened upon exposure to moisture: ν_{max} (CCl_4) 2918, 2842, 1632, 1445, 1226, 1191, 1127, 1079, 955, 844 cm^{-1}. Samples of iodo ether **27** hydrolyzed to methyl cyclohexanecarboxylate upon preparation for ^1H NMR and high-resolution mass spectroscopy.

(Dibromomethylene)cyclohexane (63). A. Preparation. According to the general procedure,[51] a solution of 24.1 g (91.8 mmol) of triphenylphosphine, 3.00 g of dry cyclohexanone, and 15.2 g (45.9 mmol) of tetrabromomethane (Eastman) in 250 mL of benzene was stirred and heated under reflux under a nitrogen atmosphere for 14 h. The reaction mixture was cooled, filtered, and concentrated on a rotary evaporator. The residue was leached with two 200-mL portions of hexane, the combined hexane solutions were filtered, and the solvent was removed on a rotary evaporator. Gas-chromatographic analysis revealed a small amount of cyclohexanone and a majority of dibromoalkene **63**, which was obtained by preparative gas chromatography (A) as a colorless liquid: ν_{max} (CCl_4) 2926, 2850, 1618, 1448, 1267, 1227, 985, 904, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (m, 4, $(CH_2)_2C{=}C$), 1.51 (m, 6, 3 × CH_2); λ_{max} (pentane) 207 (ϵ 14000), 215 (ϵ 10000), 219 nm (shoulder, ϵ 8400); λ_{max} (methanol) 208 (ϵ 12000), 214 (ϵ 10000), 220 nm (ϵ 7900). The ^1H NMR spectrum was in agreement with that previously reported.[30]

(Bromochloromethylene)cyclohexane, a minor product probably arising from chlorotribromomethane impurity in the tetrabromomethane, was obtained as a colorless liquid: ν_{max} (CCl_4) 2926, 2848, 1448, 1267, 1227, 1222, 985, 909, 829 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (m, 4, $(CH_2)_2C{=}C$), 1.51 (m, 6, 3 × CH_2); m/e 207.9651 (calcd for $C_7H_{10}ClBr$, 207.9655), 212 (7), 210 (32), 208 (25), 170 (7), 168 (27), 166 (21), 93 (43), 68 (100), 67 (32).

Removal of residual cyclohexanone from a later preparation was effected by washing the hexane solution with two 50-mL portions of 10% sodium bisulfite, filtering, and distilling (bulb to bulb) to afford dibromide **63** in a yield of 42%: bp 68–72 °C (1.0–1.2 mm).

B. Photoproducts. The following products were isolated by preparative gas chromatography from the irradiations described in Table IX.

Bromide **48**[27] was obtained as a colorless liquid which was characterized by direct comparison with the material described above.

(Bromomethoxymethylene)cyclohexane (68) was obtained as a colorless liquid: ν_{max} (CCl_4) 2927, 2851, 1652, 1448, 1258, 1231, 1195, 1132, 1083, 961, 853 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.66 (s, 3, $-OCH_3$), 2.3 (m, 4, $(CH_2)_2C{=}C$), 1.6 (m, 3 × CH_2); m/e 204.0150 (calcd for $C_8H_{13}BrO$, 204.0150), 206 (51), 204 (52), 125 (100), 93 (35), 86 (89), 68 (44), 67 (37).

(Dichloromethylene)cyclohexane (64). A. Preparation. According to the general method,[52] 250 mL of *tert*-butyl alcohol (distilled from sodium) was added to a 2-L, three-necked flask equipped with a reflux condenser, addition funnel, and a mechanical stirrer. The system was

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flushed with nitrogen, 10 g (250 mmol) of potassium was added, and the mixture was heated under reflux until all of the potassium had reacted (10 h). The reflux condenser was exchanged for a 30-cm Vigreux column, and *tert*-butyl alcohol was distilled from the reaction mixture until crystals appeared in the bottom of the reaction flask. One liter of heptane was added and the distillation was continued until the temperature at the still head had increased to 98 °C and the reaction mixture volume had decreased to 750 mL. The reaction mixture was cooled to 0–5 °C and 65.5 g (250 mmol) of triphenylphosphine was added in a single portion, followed by a solution of 29.8 g (250 mmol) of dry, alcohol-free chloroform over a period of 1 h. The reaction mixture was warmed to 15–20 °C, and the *tert*-butyl alcohol which had been produced during the reaction was distilled from the reaction mixture under reduced pressure until the reaction mixture volume had been reduced to 400 mL. The reaction mixture was cooled to a temperature below 10 °C and 49.1 g (500 mmol) of dry cyclohexanone was added in six portions over a period of 30 min. The reaction mixture was stirred for an additional 2 h at 10 °C, then for 5 h at 25 °C, and allowed to stand overnight. The reaction mixture was filtered, and the filtrate was reduced in volume on a rotary evaporator. The residue was distilled through a 25-cm Vigreux column at a gradually diminishing pressure. Gas-chromatographic analysis revealed the presence of considerable cyclohexanone; the distillate was carefully redistilled to afford 18.5 g (45%) of dichloride **64** as a colorless liquid: bp 77–79 °C (12 mm); ν_{max} (CCl_4) 2923, 2847, 1616, 1447, 1228, 986, 925, 917, 858 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (m, 4, $(CH_2)_2C{=}C$), 1.51 (m, 6, 3 × CH_2); λ_{max} (pentane) 200 (shoulder, ϵ 11 000), 204 (ϵ 12 000), 208 nm (shoulder, ϵ 11 000); λ_{max} (methanol) 207 nm (ϵ 8400). The IR and ^1H NMR spectra were in agreement with the reported values.[30,31]

B. Irradiation. From the irradiation described in Table IX, the following products were isolated as colorless liquids by preparative gas chromatography. Methylenecyclohexane (**52**) was identified by direct comparison with a commercial specimen. (Chloromethylene)cyclohexane (**69**) was identified by comparison of its spectral properties with those previously reported.[32,33]

Acknowledgment. Generous financial assistance by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Robert I. Davidson for the preparation and irradiation of iodide **39**.

Registry No. 2, 35895-37-5; **3**, 21981-08-8; **6**, 1000-86-8; **11**, 17497-54-0; **12**, 49565-03-9; **13**, 17497-53-9; **14**, 17497-52-8; **17**, 26819-54-5; **23**, 50438-51-2; **26**, 31059-39-9; **29**, 13294-30-9; **30**, 4927-03-1; **32**, 50438-50-1; **34a**, 177-10-6; **34b**, 933-40-4; **37a**, 931-57-7; **37b**, 930-66-5; **39**, 40648-08-6; **40**, 16642-49-2; **43**, 931-94-2; **44**, 930-29-0; **45**, 23904-33-8; **46**, 23904-34-9; **47**, 27784-30-1; **48**, 1121-49-9; **49**, 184-26-9; **51**, 27784-29-8; **61**, 871-28-3; **6i**, 67091-34-3; **63**, 60014-85-9; **64**, 1122-55-0; **67**, 87372-64-3; **68**, 87372-65-4.

Vancomycin: Structure and Transformation to CDP-I

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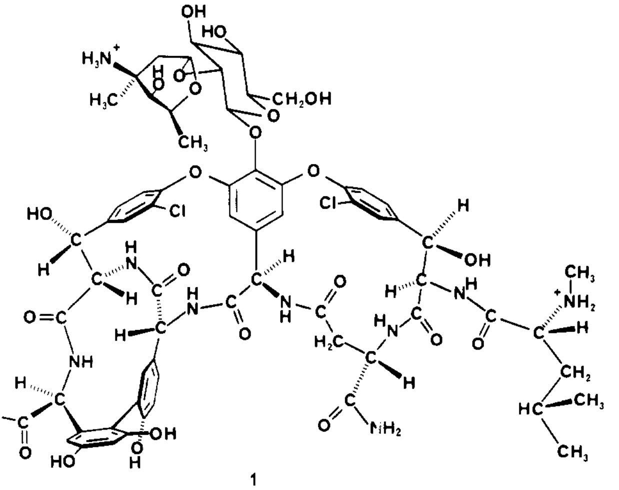
Abstract: The structure of vancomycin is assigned as **7** in which aspartate is present as asparagine, rather than isoasparagine (i.e., **4**) as had been proposed previously (Williamson, M. P.; Williams, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 6580). The mechanism of rearrangement of vancomycin to CDP-I has been investigated. The pathway is deduced: vancomycin → succinimide **11** → CDP-I-m (**3**) ⇄ CDP-I-M (**2**). Succinimide **11** has been isolated and characterized by FT-IR and FAB-MS; these data are in agreement with an in-chain succinimide but not a seco structure. Treatment of **11** at pH 8 leads to immediate appearance of the minor form of CDP-I, which slowly yields an equilibrium mixture with the major form (~64:36 of 2:3). No major change in the equilibrium ratio or rate of equilibration was found by changing solvent (H_2O, Me_2SO, or 0.1% TFA/20% 2-propanol) or pH (in the range 2.0–8.0). High-field ^1H NMR studies of **2** and **3** indicate that they are atropisomers involving different orientations of the Cl-substituted aromatic ring of residue 2, in agreement with earlier assignments by Williamson and Williams. It is concluded that **2** and **3** can interconvert by simple reorientation of the aromatic ring rather than via a transient cleavage product. The cyclophane ring in which the Cl-substituted aromatic residue 2 is embedded is enlarged by one methylene unit in the conversion of vancomycin to CDP-I; rotation of ring 2 can occur in CDP-I but not in vancomycin. The additional methylene unit in the N-terminal cyclophane ring of CDP-I causes the ring to lie in a conformation that is significantly different from that of vancomycin.

The glycopeptide antibiotic, vancomycin, first reported in 1956,[1] has received renewed attention as a therapeutic agent in recent years, both for intravenous use in the treatment of methicillin-resistant staphylococcal infections and for oral use in the treatment of *Clostridium difficile* associated colitis.[2] The structure and mode of action of vancomycin have also been the subjects of numerous investigations.[3]

The first complete structure of vancomycin (**1**) was proposed by Sheldrick et al.[4] in 1978 on the basis of three types of evidence:



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(1) chemical degradation studies that revealed the amino acids and the unusual amino sugar, vancosamine;[5] (2) high-field NMR

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