

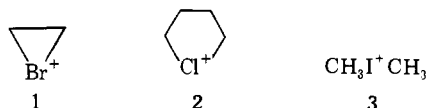
Cyclization of Mono- and Dimethylated Dihalides to Five- and Six-Membered Ring Halonium Ions

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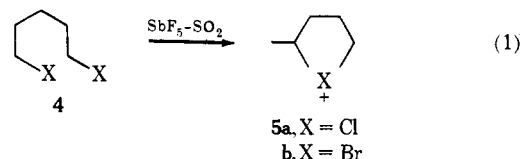
Abstract: Previous attempts to form six-membered ring halonium ions by reaction of dihalides with $\text{SbF}_5\text{-SO}_2$ gave exclusive rearrangement to five-membered ring 1-methyltetramethylenehalonium ions. In the present work, monomethylation of 1,5-diiodopentane, followed by cyclization, gave six-membered ring pentamethyleneiodonium ion containing less than 6% rearranged ion. With the same procedure, 1,5-dibromopentane gave the first observed six-membered ring bromonium ion, pentamethylenebromonium ion, contaminated with 27–45% rearranged ion. The methylating agent was $\text{CH}_3\text{F-SbF}_5$ complex in SO_2 . Dihalide (1 mol) was added to either 1 or 2 mol of $\text{CH}_3\text{F-SbF}_5$ complex in SO_2 . In the latter instance, interesting "dihalonium" ions $[\text{CH}_2\text{X}(\text{CH}_2)_n\text{XCH}_3]^{2+}$ were formed ($n = 1, 3, 4, 5, 6$) which were cyclized (when $n = 4$ or 5) by addition of an additional mole of dihalide, probably *via* the monomethylated species $[\text{CH}_2\text{X}(\text{CH}_2)_n\text{X}]^+$. Techniques were developed for recrystallizing tetramethyleneiodonium and pentamethyleneiodonium ions from $\text{SO}_2\text{-CH}_2\text{Cl}_2$ mixtures as the hexafluoroantimonate (SbF_6^-) salts. In the case of cyclic halonium ions prepared by the older procedure involving direct reaction of diiodides with $\text{SbF}_5\text{-SO}_2$, a precipitate consisting of SbI_3 and I_2 also was isolated and identified. The six-membered ring ions and dihalonium ions were characterized by their reactions with methanol and acetic acid, respectively, and by ^{13}C and ^1H nmr spectra. Stability of halonium ions as a function of ring size is discussed.

A number of cyclic halonium ions have been described as stable species in $\text{SbF}_5\text{-SO}_2$ solution, following the initial report² of the preparation of three-membered ring halonium ions, of which ethylenebromonium ion (1) is an example.³ Five-membered rings,



typified by tetramethylenechloronium ion (2), were prepared⁴ shortly after the three-membered rings were reported, and further studies have yielded additional examples having ring sizes three or five.⁵ Various dialkylhalonium ions were recently prepared, including the parent dimethylhalonium ions,⁶ typified by dimethylhalonium ions (3) obtained as the hexafluoroantimonate salt, $[(\text{CH}_3)_2\text{X}]^+\text{SbF}_6^-$.

Prior to the present work, potential precursors of six-membered ring halonium ions were observed to react with quantitative rearrangement to give five-membered rings.⁴ Equation 1 illustrates this rearrangement reaction of 1,5-dichloro- and 1,5-dibromopentane ($\text{X} = \text{Cl}$ or Br). We now report that 1,5-diiodopentane (4, $\text{X} = \text{I}$) does yield some six-membered ring iodonium ion, along with rearranged ion 5 ($\text{X} = \text{I}$) upon reaction with appropriate proportions of SbF_5 in SO_2 . A procedure has been developed for isolating and recrystallizing iodonium ions formed in this way from diiodides. However, attempts to form the analogous bromonium ion gave exclusively the previously reported analogous rearrangement product 5b (eq 1). Accordingly, a better method for preparation of cyclic halonium ions appeared to be needed if additional



examples of the six-membered rings were to be prepared and studied. We now report such a method, based on the properties of methylhaloalkylhalonium ions (*cf.* eq 2 and 3), or "dihalonium" ions obtained by monomethylation or dimethylation of dihalides. Dipositive "dihalonium" species themselves represent a new type of compound, of which we report several examples.

Nomenclature

With the proliferation of ring sizes among the halonium ions and the isolation of recrystallized salts, reported below, it seems appropriate to discuss the available nomenclature systems for this new class of heterocycle. Toward this end we have consulted with Dr. Kurt L. Loening, Director of Nomenclature, Chemical Abstracts Service. His analysis provides the basis for the following short presentation. The polymethylenehalonium ions have been used by Olah (*cf.* references herein) and by us and are approved IUPAC names. However, an extension of the Hantsch-Widman names of heterocycles (see Table I) often leads to shorter names and has already been the basis of names which have appeared in *Chemical Abstracts*. A third system of nomenclature is based on the substitution of CH_2 in the appropriate cycloalkane by the positive halogen (replacement name). Such names are used for complicated heterocycles (such as bicyclic compounds) of which at least one example has been reported in the case of halonium ions (named 3-chloronia[4.3.0]bicyclononane in Table I). Replacement names have not appeared in the literature in connection with halonium ions.

Unfortunately, different numberings apply for the different nomenclatures. For the Hantsch-Widman

(1) Postdoctoral Investigator.
 (2) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967).
 (3) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).
 (4) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).
 (5) For references, see P. E. Peterson and B. R. Bonazza, *ibid.*, **94**, 5017 (1972).
 (6) G. A. Olah and J. R. DeMember, *ibid.*, **92**, 718 (1970).

Table I. Nomenclature of Cyclic Halonium Ions

Compd	Polymethylene ^a name	Hantsch-Widman ^b name	Replacement ^c name
A	Ethylenebromonium	Bromiranium ^d	Bromoniacyclopropane
B	1,2-Dimethylethyleneiodonium	2,3-Dimethyliodiranium ^d	2,3-Dimethyliodoniacyclopropane
C	Trimethyleneiodonium	Iodetanium	Iodoniacyclobutane
D	Tetramethylenechloronium	Chlorolanium ^d	Chloroniacyclopentane
E	<i>cis</i> -1,2-Cyclohexylenedimethylechloronium	<i>cis</i> -Hexahydro-2-benzochlorolanium	8-Chloronia- <i>cis</i> -bicyclo[4.3.0]nonane
F	Pentamethyleneiodonium	Iodanium ^e	Iodoniacyclohexane
G	Hexamethyleneiodonium	Iodepanium	Iodoniacycloheptane

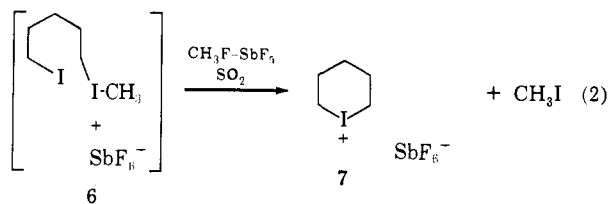
^a IUPAC: "Nomenclature of Organic Chemistry; Definitive Rules for Section C," Butterworths, London, 1965, Rules C-82, C-107.
^b IUPAC, "Nomenclature of Organic Chemistry, Definitive Rules for Sections A and B," Butterworths, London, 1966, Rule D; see also *Chemical Abstracts*, "The Naming and Indexing of Chemical Compounds," 1957, Rule 375. ^c Glossary section of IUPAC publication referenced in footnotes *a* and *b*, Rules B-4 and C-82.3. ^d Name which appears in "Chemical Abstracts Subject Index," Vol. 69 (1968).
^e Dr. Kurt L. Loening, Director of Nomenclature of the Chemical Abstracts Service, has suggested that the name might be misleading, but we have chosen the shorter name for the sake of simplicity.

and replacement systems for monocyclic rings it is appropriate to number the halogen 1. (Notice that for polycyclic systems the halogen is not necessarily numbered one in the replacement system.) For the polymethylene system, carbon was numbered one in the early papers on ethylenebromonium ions while halogen was numbered one for tetramethylene ions. It now seems reasonable that the numbering should be that of the divalent radical on which the system is based.

In the present paper we use the polymethylene system with carbon numbered one as the preferred nomenclature.

Reactions

Preparation of Halonium Ions by Methylation of Dihalides. The cyclization procedure which we have developed is typified by the reaction given in eq 2, which

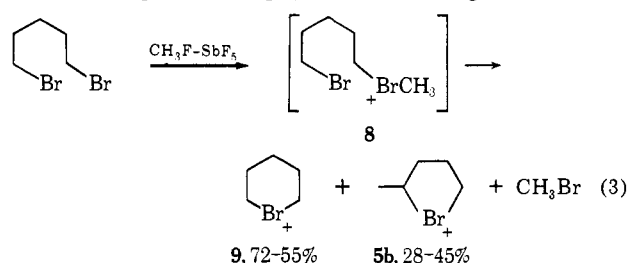


proved to be the method of choice for preparation of iodanium ion (7). The reactant 6 was not observed by nmr but is thought to have been formed *in situ* by one of several methods to be discussed. The product was contaminated with only approximately 5% of rearranged 1-methyltetramethyleneiodonium ion (5, X = I). Evaporation of the SO₂ solvent and washing with CH₂Cl₂ gave the solid white salt 7. Recrystallization of the six-membered ring compound was accomplished in the case of material prepared by direct ionization of 1,5-diiodopentane (see below). The ion could be stored indefinitely at -70°.

The most direct method for the presumed *in situ* formation of methylhaloalkyl ions analogous to 6 was the monoalkylation of the appropriate dihalide with 1 mol of CH₃F-SbF₅,⁷ the remarkable methylating agent

(7) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *ibid.*, 91, 2112 (1969).

discovered in Olah's group. The possibility that the reaction course actually involved dimethylation followed by reversion to a monomethylated ion will be discussed below. The success of this direct route is illustrated by the successful preparation of the first observed six-membered ring bromonium ion (9) from 1,5-dibromopentane (eq 3). The rearranged ion 5b was



also formed. The relative percentages of 9 and 5b ranged from 72 to 55% and 28 to 45%, respectively, in different experiments. The formation of 9 contrasts with the result of direct ionization with SbF₅ (eq 1), which is exclusive rearrangement to ion 5b. The structures of the six-membered ring ions, 7 and 9, were indicated by their hydrogen and ¹³C nmr spectra (Figures 1 and 2) and by their reaction products with methanol, described later. The nmr data are summarized in Tables II and III, with data for other ions described below.

Table II. Proton Chemical Shifts of Halonium Ions^a

Ion	δ_{TMS} , ppm			
	CH ₃ X ⁺	-CH ₂ X-	-CH ₂ CX ⁺	-CH ₂ CCX ⁺
7 ^b		4.19	1.8	1.8
9 ^b		4.89	2.1-2.5	
CH ₃ I ⁺ (CH ₂) ₄ I ⁺ CH ₃	3.42	4.38	2.33	
CH ₃ I ⁺ (CH ₂) ₅ I ⁺ CH ₃	3.40	4.38	1.9-2.6	1.4-1.9
CH ₃ I ⁺ (CH ₂) ₆ I ⁺ CH ₃	3.40	4.41	1.9-2.5	1.3-1.9
CH ₃ Br ⁺ (CH ₂) ₅ Br ⁺ CH ₃	3.90	4.85	2.0-2.5	1.4-2.5

^a Spectra were recorded on a Varian A 60-MHz spectrometer at -65° and are reported from external capillary TMS. ^b Spectra were recorded on a Varian XL100FT spectrometer internally locked to a TMS capillary.

Table III. Carbon-13 Chemical Shifts and Coupling Constants of Halonium Ions^a

Ion	δ_{CS_2} , ppm (J_{CH} , Hz)			
	$\text{CH}_3\overset{\oplus}{\text{X}}-$	$-\text{CH}_2\overset{\oplus}{\text{X}}-$	$-\text{CH}_2\overset{\oplus}{\text{C}}\text{X}-$	$-\text{CH}_2\text{C}\overset{\oplus}{\text{C}}\text{X}-$
7		157.4 (158)	168.0 (131)	167.4 (131)
9		129.9 (162)	167.4 (132) ^b	170.2 ^b
$\text{CH}_3\overset{\oplus}{\text{I}}\text{CH}_2\overset{\oplus}{\text{I}}\text{CH}_3$	173.9 (160)	193.6 (183)		
$\text{CH}_3\overset{\oplus}{\text{I}}\text{CH}_2\text{I}$	176.6 (159)	217.9 (180)		
$\text{CH}_3\overset{\oplus}{\text{I}}(\text{CH}_2)_3\overset{\oplus}{\text{I}}\text{CH}_3$	182.7 (159)	160.4 (158)	163.7 (136)	
$\text{CH}_3\overset{\oplus}{\text{I}}(\text{CH}_2)_3\text{I}$	183.5 (158)	152.5 (158)	160.8 (131)	187.6 (153) ^c
$\text{CH}_3\overset{\oplus}{\text{Br}}\text{CH}_2\text{Br}$	153.4 (162)	143.1 (190)		
$\text{CH}_3\overset{\oplus}{\text{Br}}(\text{CH}_2)_3\overset{\oplus}{\text{Br}}\text{CH}_3$	153.9 (162)	133.6 (164)	165.1 (136)	
$\text{CH}_3\overset{\oplus}{\text{Br}}(\text{CH}_2)_3\text{Br}$	155.4 (163)	126.4 (163)	161.8 (133)	162.2 (155) ^d

^a Spectra were recorded on a Varian XL100FT spectrometer at -65° . The chemical shifts are referenced to 0.8 M CS₂ in SO₂ at -55° .

^b Assignments may be reversed. ^c For CH₂I. ^d For CH₂Br.

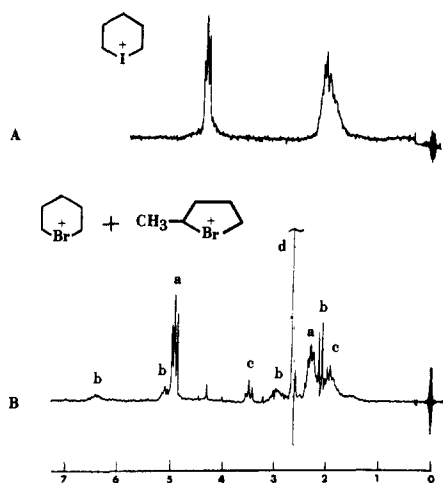
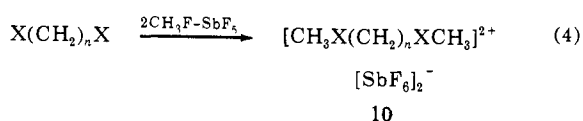


Figure 1. The 100-MHz ¹H spectra of pentamethyleniodonium ion (A) and a mixture of pentamethylenebromonium and 1-methyltetramethylenebromonium ions (B) in SO₂ at -65° , both at 2500-Hz sweep width. In spectrum B peaks of the pentamethylenebromonium ion are labeled (a), peaks of the 1-methyltetramethylenebromonium ion are labeled (b), and peaks of excess 1,5-dibromopentane are labeled (c). The large singlet at δ 2.65, labeled (d), is the CH₃Br signal.

An alternative procedure (at least from an operational standpoint) for forming cyclic ions involved the prior formation of dimethylated "dihalonium" ions, using 2 mol of CH₃F-SbF₅ complex. These new dipositive species of various chain lengths were of considerable interest not only in regard to their possible cyclization, but also because of the expected increasing charge-charge repulsion and increasing difficulty of preparation as the chain length is decreased. Accordingly, we attempted the dimethylation of a number of dihalides and obtained the dihalonium ions indicated in eq 4.



X = Br; $n = 3, 5,$ and 6

X = I; $n = 1, 2, 3, 4, 5,$ and 6

Some of these ions have been prepared in Olah's laboratory, and accordingly, we report ¹H nmr spectra

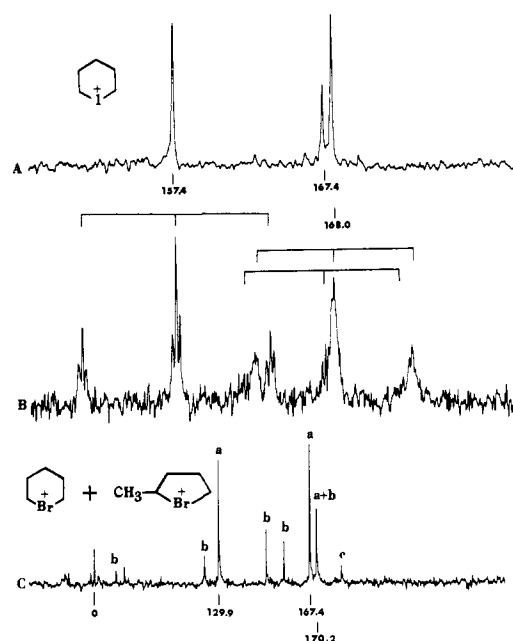


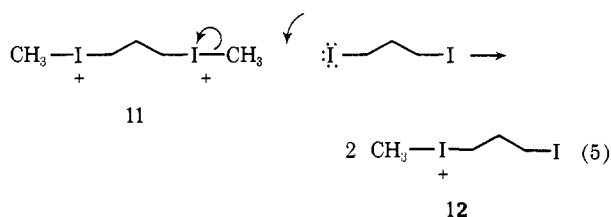
Figure 2. Noise-decoupled (A) and coupled (B) Fourier transform ¹³C spectra of pentamethyleniodonium ion in SO₂ at -65° , both at 2000-Hz sweep width; (A) 500 pulses. In spectrum C, peaks for the pentamethylenebromonium ion are labeled (a) and those for the 1-methyltetramethylenebromonium ion are labeled (b); 5000-Hz sweep width, 300 pulses. The peak at δ_{CS_2} 170.2 consists of overlapping signals for the C-4 carbon of the pentamethylenebromonium ion and the methyl group of the 1-methyltetramethylenebromonium ion. The small peak labeled (c) is the CH₃Br signal.

in Table II only for ions whose hydrogen spectra do not appear in a preprint from Olah's group received in an exchange of information.⁸ In Table III ¹³C nmr data for dihalonium ions are given, with data for other ions. As noted also by Olah's group, the formation of the dimethylated ion [CH₃ICH₂ICH₃]²⁺ from methylene iodide is of particular interest (*cf.* Figure 3). Since the ions 10 must be formed *via* the monomethylated dihalides, the clean formation of dimethylated species for $n = 4$ or 5 indicates that the second methylation occurred faster than cyclization.

Unpublished work of B. R. Bonazza in our labora-

(8) G. A. Olah, Y. K. Mo, E. G. Melby, and H. C. Lin, unpublished manuscript. We thank Professor Olah for this information.

tory indicated the likelihood that dihalides would react as nucleophiles with the dipositive ions **10** to give the monopositive haloalkylmethylhalonium ions. This result was directly verified (eq 5) in the case of the ion **11**

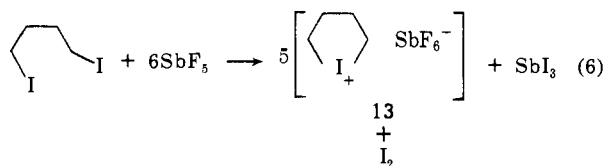


(X = I) derived from 1,3-diiodopropane. Cyclization of the resulting monomethylated ion **12** to give the strained four-membered ring and CH₃I was not observed, probably indicating that at equilibrium the acyclic ion **12** predominates, as expected. Nmr data for **12** and other haloalkylmethylhalonium ions obtained in the present study are given in Tables II and III. Included are data for monomethylated methylene iodide and methylene bromide. In contrast with the iodide, methylene bromide was not dialkylated.

In the case of dihalonium ions **10**, $n = 5$, derived from pentamethylene dihalides, addition of 1 mol of dihalide to CH₃F-SbF₅ gave, ultimately, the cyclic six-membered rings **7** or **9**. This observation provides additional evidence that the monoalkylated ions **6** and **8** are the immediate precursors to the cyclic ions. For the direct cyclization with 1 mol of CH₃F-SbF₅ (eq 3), it could be argued that dihalide is the true precursor of cyclic ion and that CH₃F-SbF₅ merely serves as a source of SbF₅, which is known to give cyclization by reaction with dihalides. For cyclization *via* dihalonium ions (eq 4 and 5), it appears impossible that SbF₅ is present in substantial amount, since it has been converted to SbF₆⁻ in the reaction of eq 4.

The postulated nucleophilic attack of halides on halonium ions (eq 5) suggested that dimethylbromonium ion also would be a sufficiently active methylating agent to form cyclic ions from the dihalides, provided equilibrium favored the cyclic species. This expectation was realized in the case of 1,5-dibromopentane. The relative per cents of unrearranged and rearranged ions **9** and **5b** were 73 and 27%, based on integration of nmr spectra.

Reaction of Diiodoalkanes with Antimony Pentafluoride. In addition to developing the above described procedure for converting dihalides to halonium ions with SbF₅-CH₃F, we have reinvestigated the direct reaction of diiodides with SbF₅ in SO₂, typified by the formation of tetramethyleneiodonium ion (**13**) (eq 6).



As shown in the equation, we found not only I₂, previously observed in similar reactions,⁶ but also SbI₃ among the reaction products. The solid SbI₃ and I₂ were separated by low-temperature filtration to give a filtrate from which the tetramethyleneiodonium hexafluoroantimonate (**13**) was obtained as a solid by evaporation of the SO₂. Recrystallization from CH₂Cl₂-

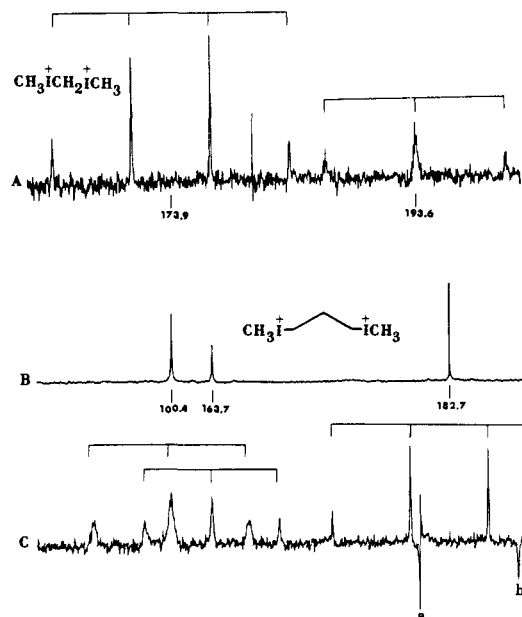
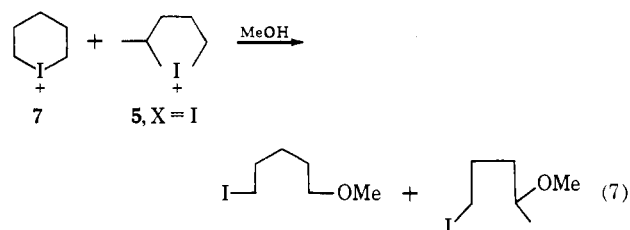


Figure 3. (A) Coupled Fourier transform ¹³C spectrum of dimethylated methylene iodide in SO₂ at -65°; 1000-Hz sweep width, 1000 pulses. (B) Noise-decoupled and (C) coupled FT ¹³C spectra of dimethylated trimethylene iodide in SO₂ at -65°; both at 1000-Hz sweep width: (B) 100 pulses and (C) 1000 pulses. In spectrum C a spurious peak (a) and a foldover of the upfield peak of the methyl quartet (b) are present.

SO₂ was accomplished to give the first crystalline cyclic halonium ion salt. Dimethylhalonium ion salts were previously obtained as apparently crystalline materials upon evaporation of solvent.⁶ The stoichiometry shown in eq 6 (1.2 molar ratio of SbF₅ to dihalide) is in approximate agreement with the experimentally determined sufficient amount of SbF₅ for complete reaction (1.4:1 molar ratio). The isolation and identification of SbI₃ as a major product represents a substantial advance, since many antimony-containing products may be envisioned. The necessity for removal of solids by filtration represents a disadvantage in preparation of ions by this procedure compared to that using CH₃F-SbF₅, as described above.

Reactions of the Halonium Ions. Pentamethyleneiodonium ion (**7**) rearranged in part to 1-methyltetramethyleneiodonium ion (**5**, X = I) after 2 hr at room temperature in SO₂. Some decomposition also occurred, as was indicated by the development of iodine color and a decrease in the total ion concentration indicated by nmr spectroscopy. Pentamethylenebromonium ion (**9**), however, rearranged smoothly to the extent of about 50% over a period of 20 min at -20°. Over a longer period, complete rearrangement occurred.

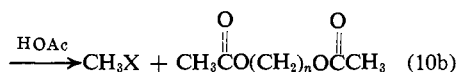
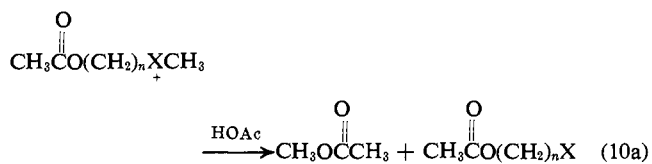
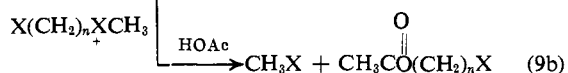
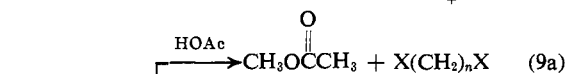
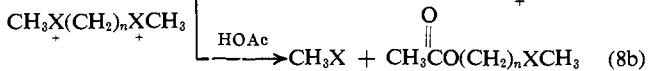
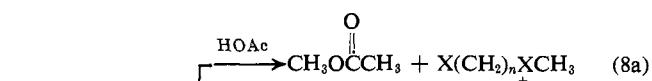
A mixture of ions **7** and **5** (X = I) reacted with methanol to give a 60% isolated yield of the ethers indicated in eq 7. There was less than 1.5% starting iodide in



the product. (Dimeric species would be expected to react to give diiodide, in part.) A mixture of the corresponding bromonium ions gave the analogous bromides.

Relative rates of attack of nucleophiles on tetramethyleniodonium ion (13) and pentamethyleniodonium ion (7) were also measured. Diethyl ether (1 mol) reacted with a mixture of 1 mol of each of the ions over a period of 2 min at 0° to result in 90% disappearance of the five-membered ring but only 30% disappearance of the six-membered ring as indicated by nmr. With 2 mol of acetonitrile, 65% of the five-membered ring but only 20% of the six-membered ring reacted over the course of 30 min. The relative rates may reflect differences in charge distributions for the two ring atoms.

It proved advantageous to characterize the methylalkylhalonium ions by their reactions with acetic acid since reaction with methanol would have given gaseous dimethyl ether as one of the products. The reactions of the dihalonium ions with acetic acid are potentially very complex, however, because of the various competing routes which the overall reaction can take (eq 8-10). For a typical monomethylated methyl-



alkylhalonium ion, attack on the methyl carbon predominated (eq 9a, $n = 3$). This observation indicated that the reaction resembles an $\text{S}_{\text{N}}2$ reaction in its selectivity (methyl > primary). Accordingly, it would be expected that only a small amount of the diacetate shown in eq 10b would be formed in the reactions of the dihalonium ions with acetic acid. In fact, a greater amount of diacetate than monoacetate was formed when $n = 3$ and $\text{X} = \text{I}$. An unusual product mixture was also found when $n = 4$ and $\text{X} = \text{I}$ in that none of the diiodide which is shown in eq 9a was found. Both of these results may be due to the fact that the intermediate ions shown in eq 8 are capable of recycling to form halonium or oxonium ions which react to give the final products.

The reactions of dimethylated and monomethylated methylene iodide were of particular interest since reaction at the CH_2 carbon would introduce a functionalized methyl group in an alkylation. Unfortunately, products which would result from such an attack were not observed in the nmr spectra of the product solutions.

Discussion

The clean rearrangement of the pentamethylenebromonium ion 9 (six-membered ring) to the 1-methyltetramethylenebromonium ion (five-membered ring) shows that the latter is substantially lower in free energy. This conclusion could not be made from the previously observed formation of five-membered rings from dihalide precursors (eq 1) because the product could have resulted from kinetic control of the course of reactions.

Although stabilization from the methyl substituent may be primarily responsible for the lower energy of the 1-methyltetramethylenebromonium ion, mentioned above, it is to be noted that the result fits into the emerging picture of three- and five-membered ring halonium ions (especially the three-membered rings) as exceptionally stable species in the absence of alkyl substituents, but subject to unusually large further stabilization when α -alkyl substituents are present. For ethylenebromonium ions (three-membered rings) stabilization by 8-18 kcal/mol (after correction for ring strain) has been estimated,⁹ based on their heats of formation in comparison with those for five-membered rings. Stabilization by methyl substitution amounts to 5 kcal/mol per CH_3 group.⁹

For five-membered rings the relative extents of possible "ring-size stabilization" and methyl substituent stabilization have not been assessed. Either of these or a combination may cause the equilibrium to lie on the side of the five-membered ring in the rearrangement reactions of six-membered ring halonium ions.

Large downfield shifts of ^{13}C nmr frequencies and high susceptibility of the chemical shifts to further deshielding upon methyl substitution suggest that the stabilizing effects mentioned above are associated with electron deficiency of the ring carbon atoms (particularly those attached to positive halogen) giving them carbonium ion character. To accommodate a variety of observations, including those mentioned above, one of us has made a suggestion (here called the odd-even postulate) that Walsh-type molecular orbitals for odd-sized rings are especially effective, compared to those of even-sized rings, in donating electrons to the vacant d orbitals of the heteroatom in cyclic halonium ions and similar molecules.¹⁰ Although the orbital symmetries of planar rings suggested the possible existence of the odd-even effect, it is entirely possible that quantitative evaluation of the orbital energies would lead to a different result from that suggested based only on one property of the orbitals and the simplifying but inaccurate assumption of ring planarity.

However, the odd-even postulate increased our interest in the nmr spectra of five- and six-membered ring halonium ions as possible indicators of the extent of charge transfer from the halo-substituted ring carbons (and possibly from their attached hydrogens) to the halogen. Accordingly, nmr parameters for the appropriate nuclei of five-membered rings¹¹ were

(9) J. W. Larsen and A. V. Metzner, *J. Amer. Chem. Soc.*, **94**, 1614 (1972).

(10) P. E. Peterson, *J. Org. Chem.*, **37**, 4180 (1972).

(11) (a) ^{13}C nmr data for five-membered ring halonium ions were obtained from unpublished work of B. R. Bonazza and P. E. Peterson. (b) Other data are from L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, pp 196-200.

subtracted from those of six-membered rings to give the values shown in Table IV. It is of interest that

Table IV. Nmr Parameters for Five-Membered Rings Subtracted from Those for Six-Membered Rings

X in (CH ₂) _{n-1} X (n = 5, 6)	CH ₂ X- parameter-		
	$\Delta\delta$ ¹³ C	ΔJ ¹³ C-H	$\Delta\delta$ ¹ H
I ⁺	13.1	2	0.42
Br ⁺	7.4	-3	0.16
S	1.2		0.19
O	-1.1		0.23 ^a
N-H	-0.5		0.01 ^a
CH ₂	-1.1	-5	0.07 ^a

^a Reference 11b.

chemical shifts for ¹³C attached to vacant d orbital atoms I⁺, Br⁺, or S are, in fact, upfield for ¹³C in six-membered rings compared to the corresponding values for ¹³C in five-membered rings (*i.e.*, $\Delta\delta$ is positive in Table IV). The opposite result occurs for ¹³C in cycloalkanes and cyclic amines and oxides, where transfer of charge to vacant d orbitals is not expected.

The above mentioned observations are suggestive of the anticipated increased charge transfer in the five-membered ring sulfide and halonium ions. For the six-membered rings, chemical shifts are similar to those for the corresponding carbons in aliphatic halonium ions, as is evident upon comparison with the data for the dihalonium ions of longer chain lengths. The observation that iodonium ions exhibit the largest $\Delta\delta$ in Table IV suggests that effects other than transfer of charge to d orbitals are involved in producing the observed chemical shifts differences, however, because overlap of Walsh type ring orbitals with halogen d orbitals would be expected to decrease with increasing size of the halogen orbitals. Conceivably, the polarizability of iodine compensates for the decreased overlap. An effect of halogen size similar to that mentioned above manifests itself when a different type of $\Delta\delta$ value is considered—the difference between the ¹³C shifts of dimethylhalonium ions [CH₂XCH₃]⁺ and their methyl halide precursors.⁶ The $\Delta\delta$ values are the following: I, 29.0; Br, 25.8; and Cl, 23.5. Again iodine acts *as if* it is the best acceptor atom. Trends for hydrogen chemical shifts (Table IV) are not so apparent as those for carbon, but the data are tabulated for the reader's inspection.

Some features of the ¹³C nmr data of Table III seem worthy of mention. The carbons remote from the halogen in the six-membered ring (δ values 168–172) are surprisingly shielded. (For cyclohexane in CCl₄, we observed δ to be 166.8 with respect to CS₂ reference.¹²) Unpublished work in our group indicates that protonated pentamethylene sulfide and pentamethylene oxide show a similar upfield shift, for which we offer no explanation. On the other hand, the CH₃X⁺ carbons of dihalonium ions and halohalonium ions show the expected further deshielding when a second electronegative group is in proximity, as in CH₃I+CH₂I+CH₃ and CH₃I+CH₂I. The position of the central carbons in CH₃I+CH₂I+CH₃, δ 193.6, and CH₃I+CH₂I, δ 217.9, may appear surprising. How-

(12) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965).

ever, these values actually show the strong upfield shift attendant upon iodine attachment to carbon (δ_{CS_2} 251.1 for CH₂I₂ in CCl₄), in combination with some normal deshielding owing to the positive charge or charges.

In our view, the observation that the five-membered ring halonium ion is attacked faster by nucleophiles than is the six-membered ring neither supports nor contravenes the postulated greater stability of the five-membered ring. If carbon atoms in the five-membered ring bear an increased positive charge compared to those in the six-membered ring, as suggested above, the experimental results are rationalized if the larger charge density for the five-membered ring increases the stability of a reactant-like transition state in which little of the extra stability of the five-membered ring is retained.

Our experiments also give information about the relative stabilities of the cyclic halonium ions relative to straight-chain halonium ions. The key to the synthetic procedure involving prior formation of methylated ions may be that cyclic five- and six-membered ring ions are more stable than are the corresponding straight-chain ions. On the other hand, unsubstituted three- and four-membered ring halonium ions probably are less stable than are the corresponding straight-chain ions since these do not react to give the cyclic species. Since the three-membered cyclic halonium ions are subject to pronounced stabilization by methyl substituents,⁹ however, highly substituted three-membered rings might, in fact, be more stable than the straight-chain species.

It was proposed above that the direct precursor of the cyclic ions is the monomethylalkylhalonium ion. This ion itself may not form in a simple fashion from the methyl fluoride-antimony pentafluoride adduct, however. In particular, most alkyl iodides have a low solubility in sulfur dioxide. Accordingly, the solid diiodide dissolves slowly in the presence of a solution containing an excess of methyl fluoride adduct. Rapid methylation at both ends of the dissolved molecules is therefore expected. Then, diiodide, slowly dissolving, may act as a nucleophile to react with the dihalonium ion to generate monomethylated ions, which then may react by an internal nucleophilic attack to generate the cyclic ions. Thus, it is likely that in cases where cyclic ions are formed in solutions of dimethylalkylhalonium ions, the actual reaction occurs *via* small amounts of the monomethylalkylhalonium ion existing in equilibrium with the dication. The monomethylated species can be generated by nucleophilic attack on the dication by some material existing as a trace impurity in the solution; indeed, sulfur dioxide itself might be a strong enough nucleophile to generate small amounts of the monomethylalkylhalonium ion in solution. Since methyl halide is produced in the cyclization step and is itself a nucleophile, a chain reaction may result once cyclization is initiated.

As explained above, methylalkylhalonium ions reacted with acetic acid to give attack primarily on methyl. One would thus expect the relative amounts of products produced from the reactions of the dihalonium ions to be dihalide > monoacetate > diacetate. Deviations from this order were found, however, for the dimethylated ions produced from 1,3-diiodopropane

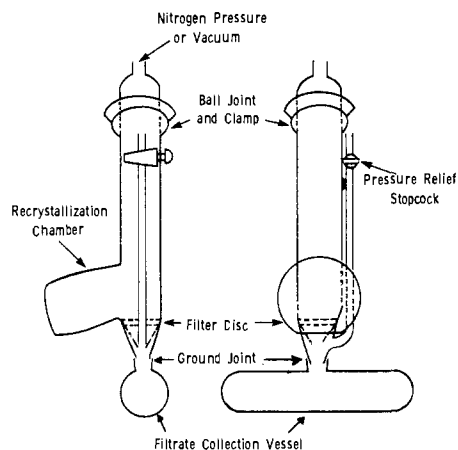
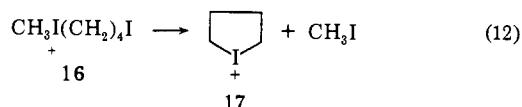
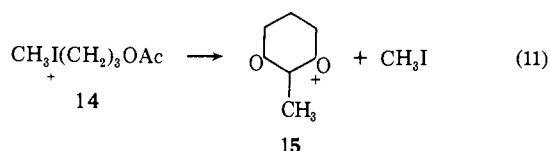


Figure 4. Apparatus used for low-temperature operations on halonium ions.

and 1,4-diiodobutane. For 1,3-diiodopropane more diacetate than monoacetate was observed, whereas for 1,4-diiodobutane no diiodide at all was found. Both of these results are explainable if additional routes of reaction which compete with those shown in eq 8–10 exist. The ions formed in eq 8 are capable of undergoing internal nucleophilic attack to form cyclic halonium and oxonium ions. The cyclic species **15** may react with acetic acid to give diacetate, whereas the ion **17** gives a monoacetate. Since the ion **14** could react by way of either eq 10a to give monoacetate or by way of eq 10b to give diacetate, the competition of eq 11 with eq 10 effectively reduces the amount of



monoacetate to be found in the product mixture. Likewise, competition of eq 12 with eq 9 reduces the amount of diiodide to be found in the final product. The kinetic problems involved in the investigation of the relative importance of the various competing reaction pathways constitute an interesting area of research in itself and is not dealt with in detail in the present work.

Experimental Section

Dihalides were obtained from Columbia Organic Chemicals Co. except for 1,3-diiodopropane which was obtained from K & K Laboratories.

Nmr. Hydrogen nmr spectra of most of the starting materials, all of the ions, and all of the products of reaction with acetic acid were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. Fourier transform ^{13}C spectra (both coupled and noise decoupled) for the ions listed in Table III were obtained on a Varian XL-100-15 spectrometer equipped with a low-temperature probe and a Varian 620i computer. Chemical shifts were obtained relative to a $\text{C}_2\text{F}_4\text{Br}_2$ capillary and were corrected to internal CS_2 by addition of 78.1 $^{\circ}$ ppm. Continuous wave 100-MHz hydrogen nmr of the iodonium ion **7**, ion **9**, the dimethylated methylene iodide, and the dimethylated propylene iodide were also obtained on this instrument.

Preparation of Ions. Ions were prepared by addition of a calculated amount of the dihaloalkane to a solution approximately 1.5 M $\text{CH}_3\text{F-SbF}_5$ in SO_2 at -65 to -78° . A ratio of 1 mol of dihaloalkane to 1 mol of $\text{CH}_3\text{F-SbF}_5$ gave a monoalkylated product, whereas a 1:2 ratio gave dialkylation in most cases. The monoalkylated product also could be obtained by addition of 1 mol of dihaloalkane to 1 mol of the corresponding dialkylated halide. Many of the diiodoalkanes exhibited only slight solubility in the $\text{CH}_3\text{F-SbF}_5\text{-SO}_2$ solution. Reaction nevertheless occurred when these solutions were warmed slightly or allowed to stand from 12 to 24 hr in a -70° cold box with intermittent stirring. The ion solutions obtained were free of solid and ranged in color from colorless to a light orange for most of the iodonium ions. The dimethylated methylene iodide and propylene iodide were isolated as white solids which could be stored at -70° for long periods of time with no sign of decomposition.

Isolation and Recrystallization of Halonium Ions. The isolation and recrystallization of tetramethylexonium ion (**13**) are described as a representative procedure. Addition of 31.6 g (13.2 ml, 0.102 mol) of 1,4-diiodobutane to 90 ml of SO_2 containing 33.3 g (0.153 mol) of dissolved SbF_5 at -70° gave a black solution in which solid SbI_3 and I_2 had formed. Overnight, orange and black solids settled leaving a yellow supernatant solution. Filtration was accomplished by precooling the apparatus shown in Figure 4 in a -70° bath, opening the upper ball joint, and pouring into it the stirred suspension of solids in SO_2 . The apparatus (Figure 4) was then tilted to the right to cause the solution to cover the sintered glass filter. The ball joint cover was replaced and the ball joint clamp tightened. Finally, the pressure relief stopcock was opened, and the apparatus was pressurized with dry nitrogen. After filtration, the vessel containing the ion solution was removed and stored at -70° . Iodine was removed from the filtered solids by washing with 50-ml portions (approximately 9) of CH_2Cl_2 at room temperature until successive washes no longer exhibited the dark I_2 color. Identification of I_2 as the likely source of color was accomplished by shaking a small portion of the $\text{CH}_2\text{Cl}_2\text{-I}_2$ with an aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution to give decolorization. Methylene chloride was removed from the red-orange solid (mainly SbI_3) remaining on the filter by passing a stream of dry N_2 through it and finally placing it under vacuum at room temperature for a short period. The weight of solid obtained was 9.9 g (11% based on SbF_5). Recrystallization from 30% benzene in CS_2 gave pure SbI_3 ; mp $169\text{--}172^{\circ}$; lit. 170° .¹⁸ Solid tetramethylexonium ion **13** was obtained as follows. The stored SO_2 filtrate was poured into the cleaned filtration apparatus immersed in a -70° bath. The relief stopcock was closed and the apparatus connected to a vacuum pump through a liquid N_2 trap. Maintaining a 1-mm vacuum for 3–4 hr resulted in removal of the SO_2 and left a brownish solid. This solid was then washed with two 40-ml portions of CH_2Cl_2 which had been pre-cooled to -70° and stored over molecular sieves (5A). (It was determined that tetramethylexonium hexafluoroantimonate was both insoluble in and unreactive with CH_2Cl_2 .) The brown color of the solid was imparted to the CH_2Cl_2 wash solution, and the remaining solid was white. The CH_2Cl_2 wash was designed to remove any unreacted 1,4-diiodobutane and also any decomposition products formed from the ion.

The filtering apparatus was removed momentarily from the -70° bath, and the filtrate collection vessel containing the CH_2Cl_2 wash solution was replaced with a clean one. The apparatus was returned to the bath and tilted to the left. A long spatula was used to move the solid on the filter into the recrystallization chamber. The -70° bath was warmed to -30° , and SO_2 was added in portions while the ion solid dissolved (~ 10 ml of SO_2). Methylene chloride was then added dropwise until the solution became cloudy (ca. 2–3 ml total). The apparatus was removed from the bath. The solution was warmed slightly until it cleared and then was replaced into the bath. The bath was then cooled to -70° over a period of 2–3 hr. Colorless needles 0.25–0.5 in. in length crystallized from the solution. The apparatus was tilted to the right, and the needles were moved to the right and separated by pressure filtration. Methylene chloride adhering to the solid was removed with nitrogen as mentioned previously. Under a nitrogen atmosphere, this solid was transferred to a glass tube with the aid of a long glass spatula and was stored at -70° . The yield of recrystallized tetramethylexonium hexafluoroantimonate was 12% (5.13 g).

Anal. Calcd for $\text{C}_4\text{H}_8\text{ISbF}_6$: C, 11.47; H, 1.93; I, 30.31;

(13) R. C. Weast, "Handbook of Chemistry and Physics," 45th ed. Chemical Rubber Co., Cleveland, Ohio, 1964.

Sb, 29.08; F, 27.22. Found: C, 11.53; H, 1.97; I, 30.28; Sb, 29.14; F, 27.35 (Galbraith Microanalytical Laboratories).

Analysis of comparable recrystallized pentamethyleneiodonium ion **7** apparently failed. The difficulty of transporting samples at Dry Ice temperature and handling of thermally unstable materials during analysis suggests that nmr spectra be relied on as evidence of structure, as has always been the case in "ion" chemistry in SbF_6^- - SO_2 . The filtrate was added to the recrystallization chamber and SO_2 was removed by evaporation under vacuum. The white solid obtained was washed with ~ 5 ml of CH_2Cl_2 , dried of CH_2Cl_2 , transferred to a glass tube, and stored at -70° . The yield was 33.2 g (79%) of unrecrystallized tetramethyleneiodonium hexafluoroantimonate. The recrystallized and unrecrystallized solids in SO_2 at -65° both gave nmr spectra identical with that previously observed for the tetramethyleneiodonium ion.⁴ The solid tetramethyleneiodonium hexafluoroantimonate (**13**) was stable at room temperatures for short periods of time but turned dark after ~ 20 – 25 min at 25° . Heating a sample for a melting point determination gave complete decomposition before melting occurred. Yields were based on dihalide as the reactant and the hexafluoroantimonate (SbF_6^-) salt of the ion as the product. For some ions, the counterion might have SbF_5 or halogen other than fluorine incorporated into it. Computing the yields in the above manner when the counterion is not SbF_6^- would tend to give calculated yields larger than the actual yields. In the calculation of yields, it was assumed that 1 mol of dihalide gave 1 mol of halonium ion. The yields were not based on SbF_5 because its stoichiometry was uncertain. Probably the largest source of yield loss occurs in the transfer of the solid ion from the filtering apparatus to the storage tube. Other halonium ion solids prepared by the method described were the tetramethylenebromonium and tetramethylenchloronium ions.

Successful preparation of pentamethyleneiodonium ion (**7**) required that the ratio of SbF_5 to diiodide be kept low in the above procedure. When the mole ratio was 1.5:1 the six-membered ring constituted about 75% of the ionic product, but when the mole ratio was 2.5:1 the five-membered ring constituted almost all of the product as indicated by nmr spectroscopy. Variation of the concentrations of the reactants in the SO_2 solution was shown not to affect the product mix.

Acetolysis of Ions. Into 10–15 ml of the SO_2 ion solution at -65° was poured 5 ml of glacial acetic acid. The resulting solution was

allowed to warm to room temperature, during which process most of the SO_2 boiled away. The room-temperature solution was poured into 20 ml of saturated NaCl solution, which was consequently extracted three times with 5-ml portions of CCl_4 . The combined organic layers were washed once with 5 ml of saturated NaHCO_3 solution and then dried over Linde Molecular Sieves (5A). Nmr spectra were taken of the starting SO_2 solutions, of the room temperature acetic acid solutions, and of the final CCl_4 solutions. Since some partitioning of the products in the various extraction layers was observed, product ratios were determined from the acetic acid solutions. Gas chromatography was done on the final solutions and was consistent with the products postulated. A Hewlett-Packard Model 5750 gas chromatograph with flame ionization detector and $1/8$ in., 6-ft stainless steel column of 10% silicone oil DC-550 on 80–100 silanized support was used.

Competitive Reaction of Tetramethylene- and Pentamethyleneiodonium Ions **13 and **7** with Nucleophiles.** Solutions of 0.70 g (0.0061 mol) of recrystallized pentamethyleneiodonium ion **7** in 3.0 ml of SO_2 (0.54 M) were added to 0.11-g (0.00025 mol) portions of **13** in nmr tubes to give total volumes of 0.5 ml. Nmr spectroscopy confirmed that the solutions were equimolar in the two ions. To one of the tubes was added 0.3 ml (0.02 g, 0.00027 mol) of diethyl ether and to another was added 0.028 ml (0.022 g, 0.00054 mol) of acetonitrile. Addition of only 1 equiv of acetonitrile resulted in the reaction being too slow to be measured conveniently. The tubes were held in an ice bath for the reaction to occur and were then examined at -65° by nmr spectroscopy after they had been re-cooled in a Dry Ice-acetone bath.

Stability Studies. The stability of the pentamethylenebromonium ion (**9**) at -20° in the A-60 nmr probe was studied. Integration of the methine proton at C-2 (δ 6.60)⁴ of the 1-methyltetramethylenebromonium ion *vs.* the sum of the bromo-substituted methylene protons next to positive bromine in the five- and six-membered rings (δ 4.8–5.2) indicated that half of the pentamethylenebromonium ion rearranged to methylated five-membered ring in *ca.* 20 min. This stability toward rearrangement is much lower than that found for the pentamethyleneiodonium ion.

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