

by a least-squares routine by using about 60 data points. The following results were obtained for fluorescence quenching of **1** by CCl₄ in benzene at 25 °C: concentration of CCl₄ (M), τ_f (ns) 0, 416; 0.087, 213; 0.247, 121; 0.870, 51.

Acknowledgment. Helpful discussions with Drs. Donald R. Arnold, Heinz D. Roth, Jay K. Kochi, and Kenneth J. Shea are gratefully acknowledged. We thank the National Science Foundation and The Robert A. Welch Foundation for financial support.

Registry No. **1**, 87373-47-5; **2**, 87433-32-7; **5E**, 83632-67-1; **5Z**, 83615-88-7; **6**, 83615-86-5; **7**, 83615-87-6; **11E**, 97012-28-7; **11Z**,

97012-29-8; **12**, 97012-26-5; **13**, 97012-27-6; **14E**, 97012-17-4; **14Z**, 97012-18-5; *cis*-**15**, 97012-11-8; *trans*-**15**, 97012-30-1; **16**, 97012-13-0; **17**, 97012-12-9; **17** (dihydro derivative), 97042-30-3; **18**, 97012-15-2; **19**, 97012-16-3; **20c**, 2717-36-4; **20t**, 6751-42-4; **21c**, 97012-21-0; **21t**, 97012-22-1; *cis*-**22**, 97012-23-2; *trans*-**22**, 97012-24-3; **23**, 97012-25-4; **24**, 83615-90-1; **27**, 49570-30-1; **30**, 2129-93-3; 1,4-CHD, 628-41-1; 1,3-CHD, 592-57-4; DBO, 3310-62-1; Ph₂S(OC(CF₃)₂Ph)₂, 32133-82-7; Ph₃PC₃H₇-n⁺Br⁻, 6228-47-3; *p*-C₆H₄(OCH₃)₂, 150-78-7; PhCl, 108-90-7; PhCCl₃, 98-07-7; *p*-C₆H₄(CN)₂, 623-26-7; PhCN, 100-47-0; CBr₄, 558-13-4; cyclopropyl bromide, 4333-56-6; 1,4-cyclohexanedione, 637-88-7; *N*-methyltriazolinedione, 13274-43-6; 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one, 69225-59-8; 3,3-dimethyl-9-propylidene-7,5-dioxaspiro[5.5]undecane, 97012-14-1; (*Z,Z*)-1,4-dipropylidene-cyclohexane, 97012-19-6; (*E,E*)-1,4-dipropylidene-cyclohexane, 97012-20-9; cyclohexanone, 108-94-1; 4-chlorocyclohexanol, 30485-71-3; 4-chlorocyclohexanone, 21299-26-3.

(100) We thank Prof. Peter B. Dervan for obtaining these spectra.

Onium Ylide Chemistry. 4.¹ Alkylhalonium Methylides

George A. Olah,* Hans Doggweiler, and Jeff D. Felberg

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089. Received July 2, 1984. Revised Manuscript Received April 20, 1985

Abstract: Alkylhalonium methylides were generated by two independent routes, proving their formation through derived product analysis. The reaction of singlet methylene, produced by photolysis of diazomethane, with methyl and ethyl halides gives in competition with C-H insertion evidence of methylenation of the halogen atom, i.e., alkylhalonium methylide formation. The unstable halonium methylides are immediately protonated or alkylated in the reaction medium to give dialkylhalonium ions which then undergo cleavage to the corresponding alkyl halides. Methylidonium methylide was also generated via the deprotonation of dimethylidonium hexafluoroantimonate with sodium hydride in competition with the expected methylation of fluoride and hydride, giving the major products. Subsequent methylation of the methylidonium methylide by excess dimethylidonium ion gives methylethylidonium ion followed by cleavage leading to the formation of ethyl halides and via hydride reduction to ethane, respectively. Attempted formation of alkylhalonium methylides via fluoride cleavage of methyl[(trimethylsilyl)methyl]halonium hexafluoroantimonates was unsuccessful due to ready disproportionation of the halonium ions.

Karele and Neilands have reported the preparation of arylidonium ylides from active methylene compounds and iodosobenzene.^{2a} Hayashi later improved the method for generating arylidonium ylides and studied the thermal and Cu-catalyzed decomposition of these iodonium ylides.^{2b} Halonium ylides have been proposed as intermediates in the formation of benzoquinones from the photolysis of 3,5-diisobutylbenzene 1,4-diazooxide with bromophenols,^{3a} isopropyl bromide,^{3b} or iodobenzene.^{3b} Several other stable arylhalonium ylides have been prepared.⁴

Chloronium ylides have been suggested as intermediates in the photochemical addition of ethyl diazoacetate in chloro-substituted methanes.⁵ The alkoxy-carbonylcarbene was proposed to attack a chlorine atom of the substituted methane solvent leading to the chloronium ylide which then undergoes intramolecular rearrangement, probably involving a radical pair. This mechanism

was later supported by ¹³C CIDNP studies.^{6a} Roth has described the abstraction of chlorine by singlet methylene from chloroform to proceed through a singlet radical pair, as evidenced by CIDNP.^{6b}

Olah et al. reported the first generation of methylhalonium methylides as reaction intermediates in the hydrogen-deuterium exchange of the corresponding dimethylhalonium ions in deuterated sulfuric acid.⁷

In our continued study of reactive onium ylide intermediates, we report here a mechanistic study of the generation of alkylhalonium ylides via two independent routes, proving their formation through derived products (albeit being by necessity in instances only minor ones).

Results and Discussion

Reaction of Methylene with Alkyl Halides. The gas-phase reaction of methylene with methyl chloride^{8a} takes place pre-

(1) For part 3, see: Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2116.

(2) (a) Karele, F.; Neilands, O. *J. Org. Chem. USSR (Engl. Transl.)* **1968**, *4*, 1755 and references therein. (b) Hayashi, Y.; Okada, T.; Kawanishi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2506.

(3) (a) Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, *90*, 3598. (b) Pirkle, W. H.; Koser, G. F. *Tetrahedron Lett.* **1968**, *36*, 3959.

(4) Frederick, K.; Amann, W. *Tetrahedron Lett.* **1973**, *38*, 3689. Kokil, P. B.; Nair, P. M. *Tetrahedron Lett.* **1977**, *47*, 4113. Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, *95*, 2695.

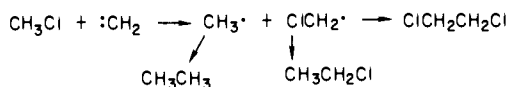
(5) Migita, T.; Ando, W.; Kondo, S.; Matsuyama, H.; Kosugi, M. *Nippon Kagaku Zasshi* **1970**, *91*, 374.

(6) (a) Iwamura, H.; Imahashi, Y.; Oki, M.; Kushida, K.; Satoh, S. *Chem. Lett.* **1974**, 259. (b) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

(7) Olah, G. A.; Yamada, Y.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 680. See also: Olah, G. A. "Halonium Ions"; Wiley-Interscience: New York, 1975.

(8) (a) Setser, D. W.; Litrell, R.; Hassler, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 2062. Johnstone, R. S. B.; Wayne, R. P. *Nature (London)* **1966**, *211*, 1396. Bamford, C. H.; Casson, J. E.; Wayne, R. P. *Proc. R. Soc. London, Ser. A* **1966**, *289*, 287. (b) Lee, P. S. T.; Rowland, F. S. *J. Phys. Chem.* **1980**, *84*, 3243.

dominantly by chlorine or hydrogen abstraction, giving rise to methyl and chloromethyl radicals. In the case of methyl chloride



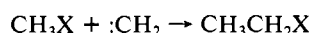
at pressures above 50 mm, the products were 30% ethane, 43% ethyl chloride, and 27% 1,2-dichloroethane, formed by radical recombination.

At lower pressures due to elimination of HCl from "hot" haloalkane molecules, ethylene and vinyl chloride are also formed. Addition of oxygen completely suppresses product formation, indicating that direct insertion is a negligible process. In these experiments, methylene was generated by photolysis of ketene and thus was a mixture of both triplet and singlet species. Recently, the corresponding tritiated system has been studied and indicates that singlet methylene abstracts halide whereas triplet methylene abstracts deuterium (from CD_3Cl) in the gas phase.^{8b}

Evidence for C-Cl insertion by methylene in the liquid phase is available.⁹ Few alkyl bromides were reacted, but apparently they react like the chlorides.^{9a,d}

In order to study the mechanism by which methylene reacts with alkyl halides in the liquid phase we photolyzed diazomethane or deuterated diazomethane in methyl and ethyl halides.

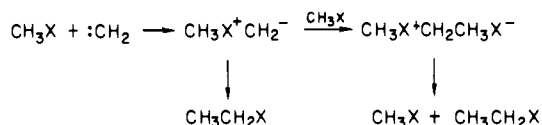
Methyl chloride, bromide, and iodide when photolyzed with diazomethane after transferring gaseous diazomethane¹⁰ into the neat methyl chloride and bromide at -78°C (iodide at -60°C) gave the corresponding ethyl halides as the main reaction product.



Some ethane and 1,2-dihaloethanes (generally less than 5% of ethyl halides) are also formed, but this is considered to be the product of a limited competing gas-phase reaction in the system above the liquid phase.

As diazomethane is generated in aqueous solution, the distilled diazomethane (bp -24°C) inevitably always contained trace impurities of dimethyl ether (bp -25°C) resulting from the reaction of methylene with water. Indeed, small amounts (<1.0%) of dimethyl ether were observed after all photolysis experiments. Furthermore, ethylene was also formed as a gaseous byproduct of the reactions. Olefin formation due to dimerization of carbenes in the photolysis of diazoalkanes is frequently observed.¹² Thus, the trace amounts of dimethyl ether and ethylene are derived from methylene itself and not associated with the alkyl halide reaction. They are consequently not included in further discussion of products.

Whether the reactions involve only direct C-H (or C-X) insertion or intermediate methylhalonium methylide formation also takes place (reaction of singlet methylene on the nonbonded electron pairs of the halogens) is not easily differentiated. The highly reactive ylides would be expected to undergo intramolecular Stevens rearrangement or more probably be methylated by excess methyl halide to the corresponding methylethylhalonium ions which then in turn would give the corresponding ethyl halides



The above reaction using CD_2N_2 yields ethyl- d_2 halides as the major products. Regardless of which mechanistic pathway is

Table I. Reaction of Methylene with Ethyl Halides ($\text{C}_2\text{H}_5\text{X}$)^a

	halide (X)		
	I	Br	Cl ^c
conversion (%) ^b	6.0	1.3	0.8
CH_3X	6.4	27.2	27.7
$(\text{CH}_3)_2\text{CHX}$	10.2	27.4	22.9
$\text{CH}_3(\text{CH}_2)_2\text{X}$	83.4	45.4	49.4
$\text{C}_2\text{H}_5\text{OCH}_3$	trace ^d	trace ^d	trace ^d
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	trace ^d	trace ^d	trace ^d

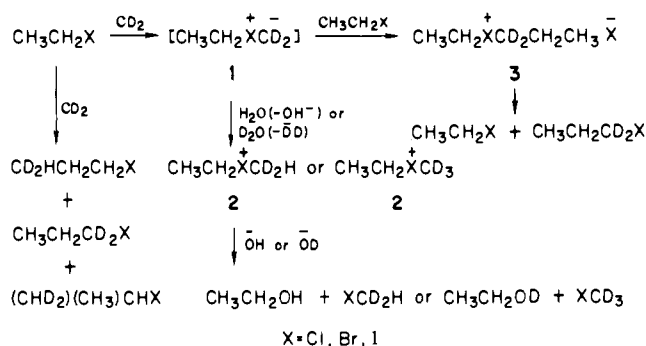
^a All values in mol %. ^b Based on ethyl halide. ^c A control experiment with added water resulted in 36.9% CH_3X , 23.3% $(\text{CH}_3)_2\text{CHX}$, and 39.8% $\text{CH}_3(\text{CH}_2)_2\text{X}$ in 0.7 conversion (%). ^d Trace <0.1%.

Table II. Deuterium Distribution^a in Methyl Halides^b from the Reaction of Ethyl Halides with CD_2 :

	halide		
	I	Br	Cl
% d_3 ^c	4.5	3.6	4.2
% d_2	75.9	55.2	64.0
% d_1	12.1	21.9	18.7
% d_0	7.5	19.3	13.1

^a Calculated from mass spectra assuming no isotope effect. ^b Detected in reaction mixture after photolysis. ^c The d_3 isomer is formed via deuteration of the ylide **1** by traces of D_2O present in the CD_2N_2 (see Scheme I).

Scheme I



followed (intermediate ylide formation or direct insertion), the same label content in the ethyl halide product must be formed; thus analysis of products in this case did not help to differentiate the two possible pathways.

This is, however, not the case when ethyl halides are reacted with singlet methylene in their photolysis with diazomethane.

The reaction of singlet methylene with ethyl chloride, ethyl bromide, and ethyl iodide was studied by transferring gaseous diazomethane¹⁰ or diazomethane- d_2 ¹¹ into neat liquid ethyl halide at -78°C followed by photolysis at around 0°C . A typical product distribution obtained from the photolysis is shown in Table I.

The products obtained from the reaction of methylene with ethyl halides are those resulting from methylene insertion into the C-H and C-X bonds (2-propyl halide and 1-propyl halide) as well as significant amounts of methyl halides and trace amounts of methyl ethyl and diethyl ether. Previously Franzen has reported the formation of small amounts of methyl bromide from the reactions of ethyl bromide and isopropyl bromide with methylene.^{9a} Franzen did not, however, consider the mechanism by which methyl bromide was being formed.

In order to study the mechanism by which methyl halide is being generated, deuterium-labeled diazomethane was employed. When diazomethane- d_2 was used in the reactions with ethyl halides, the methyl halides formed consisted primarily of the d_2 -labeled species as shown in Table II. This result can be explained only by competing attack of methylene- d_2 on the halogen atoms, forming the intermediate ethylhalonium methylides **1** as shown in Scheme I (in competition with direct C-H or C-X insertion).¹³ Halonium

(9) (a) Franzen, V. *Justus Liebigs Ann. Chem.* **1960**, 627, 22. (b) Bradley, J. N.; Ledwith, A. *J. Chem. Soc.* **1961**, 1495. (c) Meerwein, H.; Disselnkötter, H.; Rappen, F.; Rintelen, H. V.; Vloed, H. *Justus Liebigs Ann. Chem.* **1957**, 604, 15. (d) Urry, W. H.; Eisznes, J. R. *J. Am. Chem. Soc.* **1952**, 74, 5822.

(10) Dessaux, O.; Durend, M. *Bull. Soc. Chim. Fr.* **1963**, 41.

(11) Hecht, S. M.; Kozarich, J. W. *Tetrahedron Lett.* **1972**, 1501.

(12) Wulffmann, D. S.; Linstrumelle, G.; Copper, C. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Part 2, p 912.

Table III. Deuterium Distribution^a in *n*-Propyl Halides^b from the Reaction of Ethyl Halides with CD₂:

	halide		
	I	Br	Cl
%d ₂	82.4	77.2	68.5
%d ₁	11.8	12.7	22.9
%d ₀	5.8	10.1	8.5

^a Calculated from mass spectra assuming no isotope effect.^b Detected in reaction mixture after photolysis.

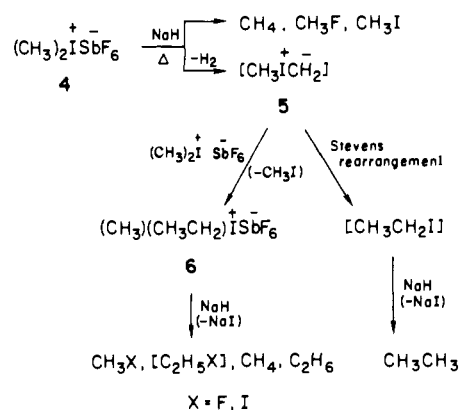
ylides **1** are then immediately alkylated by excess ethyl halides or protonated by traces of moisture in the system, forming the corresponding methylethyl- or ethylpropylhalonium ions **2** and **3**. Dialkylhalonium ions are known to be good alkylating agents;⁷ thus the halonium ions **2** and **3** can readily form dilabeled methyl or 1-propyl halides via ethylation of OH⁻ or X⁻, respectively. The latter reaction is indicated by the high ratio of 1- to 2-propyl halides (see Table I). No ethyl alcohol could be detected by using the GC conditions applied. Ethyl alcohol, however, can also further react with methylene via O-H insertion to form the methyl ethyl ether observed. It should be noted that the generation and subsequent cleavage of the halonium ylides is analogous to the cleavage pathway postulated in our preceding study of dialkylxonium methylides when generated in a similar fashion.¹

A control experiment was performed in which a small quantity (~0.005 mol) of water was added to the ethyl chloride-diazomethane solution immediately before photolysis. This resulted in increased formation of methyl chloride in comparison to the amount obtained previously (see Table I, footnote c). This observation is consistent with the mechanism shown in Scheme I wherein protonation of halonium ylides **1** by moisture leads to formation of methyl halides.

Table II also indicates that d₀ and d₁ deuterium-labeled methyl halides are being formed. This isotopic distribution arises due to the less than 100% isotopically pure diazomethane used. Indeed, the deuterium distribution found in the C-H insertion product, i.e., *n*-propyl halide, corresponds to the isotopic purity of diazomethane. As shown in Table III, approximately the same ratio of d₂:d₁:d₀ was found in the C-H insertion product as in the cleavage product, i.e., methyl halide (see Table II). Thus, the methylethylhalonium ion does not appear to be undergoing appreciable H-D scrambling before reacting to form the methyl halide.

Deprotonation of Dimethyliodonium Hexafluoroantimonate. The second route to generating alkylhalonium methylides involves the deprotonation of the corresponding methylhalonium ions with a suitable base. As dimethyliodonium hexafluoroantimonate can be isolated as a stable salt, it was possible to study its deprotonation with sodium hydride. The reaction was carried out by mixing the two salts and then carefully warming them, thus avoiding any solvent interaction. In a typical reaction of dimethyliodonium hexafluoroantimonate with excess sodium hydride, besides methyl fluoride and methyl iodide in a 4-to-1 ratio was also formed about 2-5% of methane and ethane in a 5-to-1 ratio. The formation of methyl fluoride and methyl iodide clearly comes from the decomposition via methylation of fluoride (from SbF₆⁻) of the dimethyliodonium ion. The higher amount of methyl fluoride formed is due to halide exchange between methyl iodide and antimony pentafluoride. Methane is formed by intermolecular methylation of hydride. It is the formation of ethane involving a C₁ → C₂ transformation which is the significant result of the experiment and for which we propose the pathway shown in Scheme II.

(13) A free radical pathway, such as that proposed by Urry and Eiszner for the reaction of carbon tetrachloride with methylene,^{9d} cannot be used to explain the formation of methyl halide observed in this study. This mechanism can be ruled out because of the absence of any radical recombination products (i.e., *n*-butane or 1,2-dihaloethane), and the reaction was not inhibited by added antioxidant (diphenylamine) as was reported for the radical processes studied by Urry and Eiszner^{9d} (see Experimental Section). This does not exclude, however, the possibility that the ylide **1** could give a single radical pair.

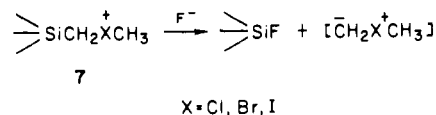
Scheme II

Proton abstraction from dimethyliodonium ion **4** forms, competing with methylation of H⁻ and F⁻, the methyliodonium methylide **5**. The ylide **5** can then either be intermolecularly methylated by excess dimethyliodonium ion **4** forming methyl-ethylhalonium ion **6** or could undergo intramolecular Stevens rearrangement forming ethyl iodide.

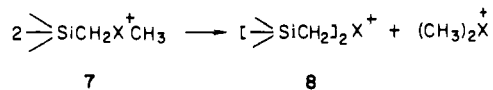
No attempt was made to differentiate these possibilities with the use of CH₃I¹³CH₃, as the analytical difficulties to analyze isotopically labeled ethanes are substantial (large error limits due to the interference of N₂ and O₂ in MS analysis). However, our studies on related oxonium and sulfonium ylides make the Stevens rearrangement or other radical pathways less probable.¹⁴ Reaction of hydride with **6** gives, besides the corresponding methyl halides, methane and ethane. No ethyl halide was observed, but methyl and ethyl halides with sodium hydride can undergo reduction to give the parent hydrocarbons. While a radical process for the formation of ethane cannot be completely ruled out, such a process seems also unlikely in view of insensitivity of the reaction system to oxygen.

Attempted Fluoride Cleavage of Methyl[(trimethylsilyl)methyl]halonium Ions. As a further approach to generating dialkylhalonium ylides, we also attempted the fluoride ion-induced desilylation of methyl[(trimethylsilyl)methyl]halonium ions.

Halonium ions **7** were prepared at low temperatures (-78 °C) in SO₂ solution by methylating the corresponding halomethyl-trimethylsilanes with CH₃F/SbF₅.¹⁵ Attempted isolation of the



halonium ions with gradual warming to room temperature lead to rapid disproportionation



Reaction with CsF lead only to alkylation products, i.e., >SiCH₂X and CH₃X (where X = F, Cl, Br, and I) in accordance with the disproportionation reaction.

Conclusions

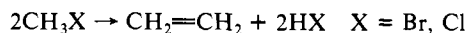
In conclusion, the elusive alkylhalonium methylides were intermediately generated through two independent routes. The first involves the reaction of singlet methylene, generated by the photolysis of diazomethane, with ethyl halides, where products indicate besides direct insertion competing attack on halogen leading to alkylhalonium methylides.

A second method involves base-induced deprotonation of dimethyliodonium hexafluoroantimonate with resultant formation

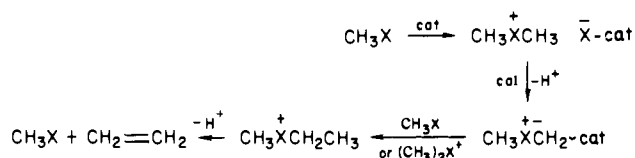
(14) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* **1984**, *49*, 2112.

(15) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.*, submitted.

of the corresponding methylhalonium methylide. Methylhalonium methylides, as shown in our preceding work, play a key role in the bifunctional acid-base-catalyzed condensation of methyl halides to ethylene



involving the following pathway¹⁶



Experimental Section

a. Reaction of Methylene with Alkyl Halides. Gaseous diazomethane was prepared by treating *N*-nitrosomethylurea with 80% potassium hydroxide solution under exclusion of light at 0 °C.¹⁰ The diazomethane was then passed through potassium hydroxide pellets under an argon stream and transferred into the cooled methyl or ethyl halide (generally -78 °C). Diazomethane-*d*₂ was prepared by the reaction of sodium deuteriooxide with *N*-nitrosomethylurea in dimethoxyethane/D₂O¹¹ and transferred by a stream of argon directly into the corresponding ethyl halide.

A solution of diazomethane or dideuterated diazomethane (prepared from 0.3 g of *N*-nitrosomethylurea) in the corresponding alkyl halide (1 mL) in a reaction tube equipped with a reflux condenser (cooled to -78 °C) was irradiated with a 275-W Sylvania Sunlamp. The apparatus was covered with aluminum foil to ensure that only the liquid phase was exposed to light. After the run was complete (indicated by the disappearance of the yellow color, usually 30 to 60 min), the reaction mixture was cooled to -78 °C in order to condense the low-boiling products and then analyzed by GC and GC/MS. A solution of diazomethane (prepared from 0.3 g of *N*-nitrosomethylurea) in ethyl chloride (1 mL) and

0.05 g of diphenylamine was illuminated as above. Analysis of the reaction mixture indicated a product distribution for the reaction of methylene with ethyl halide comparable to that shown in Table I.

b. Reaction of Dimethyliodonium Hexafluoroantimonate with Sodium Hydride. (CH₃)₂I⁺SbF₆⁻ was prepared by reacting methyl halide in SO₂ with CH₃F/SbF₅ in SO₂ at -78 °C.¹⁷ Removal of SO₂ gave the dimethyliodonium salt in high purity. Sodium hydride (Alfa, 61% mineral oil dispersion) was washed 3 times with pentane followed by heating under vacuum till all traces of hydrocarbons were removed.

One millimole of the dimethyliodonium salt and 10 mmol of sodium hydride were thoroughly mixed under argon atmosphere in a flask cooled to -78 °C. The flask was then connected to a cold trap (-78 °C) and closed with a rubber balloon in order to prevent any gaseous products from escaping. The salt mixture was then mildly heated in order to initiate the reaction. Samples of condensed and gaseous products were analyzed by GC and GC/MS.

c. Preparation of Methyl[(trimethylsilyl)methyl]halonium Hexafluoroantimonates and Their Attempted Reaction with CsF. The corresponding halomethyltrimethylsilane in SO₂/ClF was mixed with an equimolar amount of SbF₅/CH₃F in SO₂ at -78 °C. Attempted isolation of the halonium salts lead to disproportionation as indicated by NMR analysis. Reaction with CsF gave only fluoride alkylation products.

d. Analysis. GC analysis of the reaction mixture was conducted on the following instruments: (a) Varian 3700 with an OV 101 glass capillary column (50 m); (b) Hewlett-Packard 5130A with a Poropak Q column (12 ft by 1/8 in.). All percentage numbers are corrected for FID response factors and are given in mol %.

MS data of gas samples were obtained by using a Hewlett-Packard 5985Aa GC/MS system equipped with a Poropak column.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. Iodoethane, 75-03-6; bromoethane, 74-96-4; chloroethane, 75-00-3; methylene, 2465-56-7; diazomethane, 334-88-3; dimethyliodonium hexafluoroantimonate, 28021-80-9.

(16) Olah, G. A., et al. *J. Am. Chem. Soc.* 1984, 106, 2143.

(17) Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *J. Am. Chem. Soc.* 1974, 96, 3565.

Long Bonds in Cation Radicals of Vicinally Difunctional Molecules

Dennis J. Bellville, Raul A. Pabon, and Nathan L. Bauld*

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received December 18, 1984

Abstract: Ab initio theoretical studies suggest a unique stabilizing effect of vicinal electron donor substituents on long bond cation radical structures. Although cation radicals of amines appear to be of the aminium salt type, with the cation radical character largely localized on nitrogen, the calculated structural minimum of the 1,2-ethanediamine cation radical is a long bond structure which lies 11 kcal below the best localized (aminium salt) type structure. Despite powerful stabilization of the dissociated aminomethyl cation and radical, the long bond maintains substantial bond strength ($D = 23$ kcal).

Theoretically predicted structures of alkane cation radicals are characterized by a unique valence, the elongated, one-electron bond (long bond).¹⁻⁵ The optimum length calculated for the carbon/carbon bond of the ethane cation radical, for example, is 1.920 Å,³ and the dissociation energy is 43 kcal mol⁻¹.^{4,5} More complex alkane cation radicals appear to have one such long bond in which the SOMO (single occupied MO) and the "cation radical character" are rather highly localized.^{4,5} Recognition of such long

bond structures has already proved fruitful in both vapor phase (e.g., mass spectrometric⁶) and solution (e.g., cycloaddition⁷) chemistry of cation radicals. Recent theoretical research has further suggested that ground state long bond structures may be found for cation radicals of such functionalized organic molecules as alcohols, ethers, and halocarbons.⁴ However, cation radicals of molecules containing relatively more ionizable functional groups, such as alkenes, arenes, aldehydes, ketones, amines, and sulfides were predicted generally to have their cation radical sites essentially localized on the ionizable functionality (n or π type cation

(1) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* 1969, 50, 654.
 (2) Pople, J. A.; Lathan, W. A.; Curtiss, L. A. *J. Am. Chem. Soc.* 1971, 93, 808.
 (3) Richartz, A.; Bunker, R. J.; Bruna, P. J.; Peyerimhoff, S. D. *Mol. Phys.* 1977, 33, 1345.
 (4) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* 1982, 104, 294.
 (5) Borima, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* 1983, 23, 21.

(6) Wendelboe, J. F.; Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* 1981, 103, 2333.

(7) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* 1977, 99, 1291.