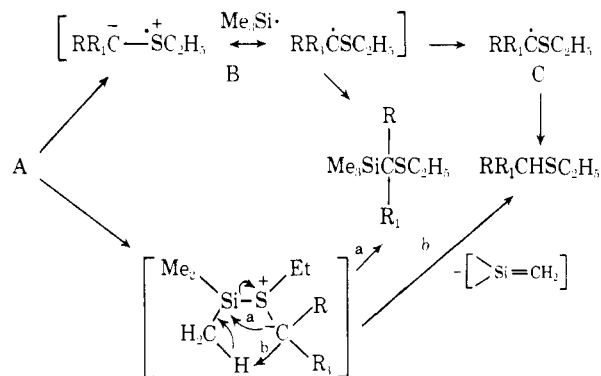


a heteroatom is a well-known reaction in carbene chemistry,^{5,8-10} an attractive mechanism for the formation of an insertion product may involve sulfonium ylide formation (A) followed by a 1,2-migration of the silyl group involving a geminate radical pair intermediate (B), which collapses to II.¹¹⁻¹³ The radical (C) which escaped the geminate pair provides, *via* hydrogen abstraction reaction, the product III. However, no evidence exists for the mechanism cited save that it may account for the products. The geminate ion pair mechanism has never been established for 1,2-migration of the silyl group. A concerted 1,2-migration of the



trimethylsilyl group might be involved in these reactions since silicon may expand its valence shell (d orbitals of appropriate symmetry are available to stabilize the transition state or intermediate for such rearrangement) (process a), and the eliminative decomposition of sulfonium ylide (A), *via* a concerted five-member cyclic transition state,^{13,14} led to the product III and [$>\text{Si}=\text{CH}_2$], the fate of which is unknown (process b).

The 1,2-migration of the silyl group from the oxonium site to carbon center may also take place in the reaction between carbenes and alkoxytrimethylsilanes. Irradiation of ethyl diazoacetate in alkoxytrimethylsilanes gave three major products, IV, V, and VI. Product VI may be rationalized in terms of C-H insertion of carbene-ethoxycarbene. The products IV and V are quite analogous to those which were obtained in the reaction with ethylthiotrimethylsilane. These products are apparently formed through a trimethylsilyloxonium ylide intermediate (D) followed by 1,2-migration of the trimethylsilyl group in either anion or radical.

1,2 Oxygen-carbon silyl group rearrangement in the reaction of phenylcarbene with methoxytrimethylsilane

(8) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971.

(9) M. Jones, Jr., and R. A. Moss, "Carbenes," Vol. I, Wiley, New York, N. Y., 1973.

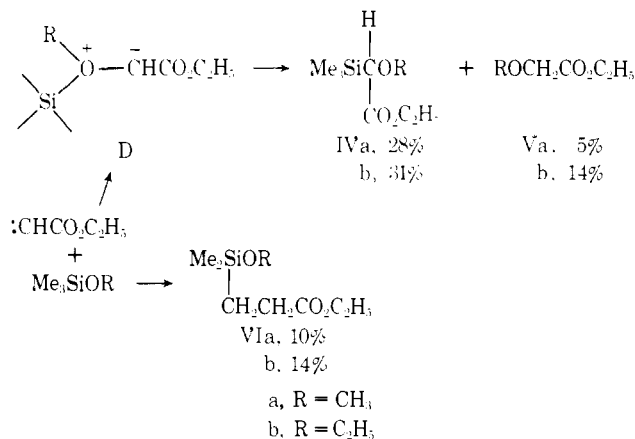
(10) Direct insertion of carbenes into the Si-S bond is considered and is also considered likely into Si-H and Si-Cl bonds in some cases. However, the reactivities of the carbene into Si-H and Si-Cl bonds were not even favored over addition on olefin, but ylide formation on sulfur was found to be more rapid than addition on olefin, especially by an electrophilic carbene. Direct insertion may not be involved in these reactions. See ref 5 and D. Seyferth, J. M. Burlitsch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, **7**, 405 (1967).

(11) U. Schöllkopf, G. Ostermann, and J. Schössing, *Tetrahedron Lett.*, 2619 (1969).

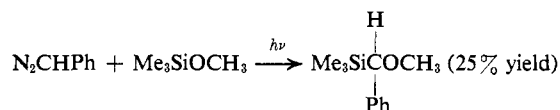
(12) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

(13) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, **37**, 1721 (1972).

(14) W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1983 (1969).



was observed to give the insertion product of phenylcarbene into the Si-O bond in 25% yield;¹⁵ the product was identified by comparison of its spectra with those of an authentic sample.¹⁶



Acknowledgment. We thank the Shinetsu Chemical Co. for a gift of trimethylchlorosilane.

(15) A few per cent of benzyl methyl ether was also obtained in this reaction.

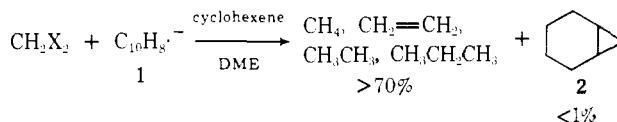
(16) An authentic sample was prepared by the reaction of phenyltrimethylsilyldiazomethane with methanol.⁷

Wataru Ando,* Kenji Konishi
Tsuneeo Hagiwara, Toshihiko Migita
Department of Chemistry, Gunma University
Kiryu, Gunma 376, Japan
Received October 29, 1973

Reaction of Sodium Naphthalene with Methylene Halides. The Methylene Radical Anion

Sir:

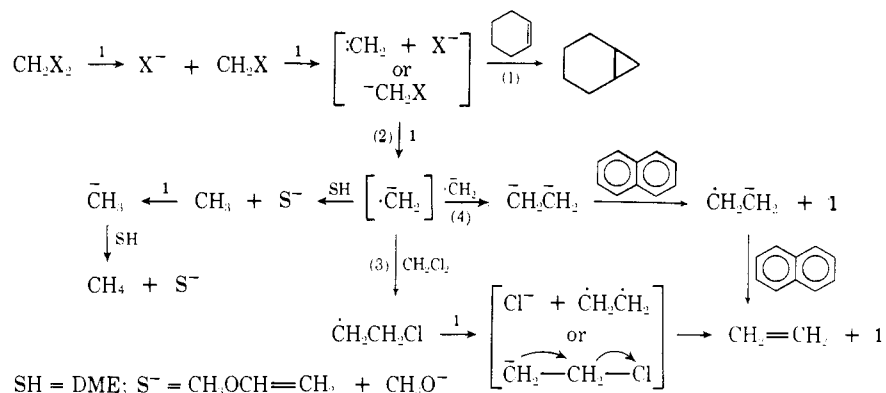
Alkyl geminal dihalides which possess β - or γ -hydrogens react with sodium naphthalene (1) to yield products of C-H insertion. These reactions reveal the intervention of a carbene (or carbenoid) intermediate.^{1,2} Treatment of the methylene halides CH_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) should thus give methylene (or its carbenoid counterpart), which could be detected by its addition to an olefinic double bond.² In fact, reaction of 1 *M* CH_2Cl_2 in 60:40 (v/v) cyclohexene-1,2-dimethoxyethane (DME) with excess 1 *M* sodium naphthalene does yield norcarane, but in yields of less than 1%. The principal products of the reaction (>70%) are low molecular weight hydrocarbons. Alkylated naphthalenes and dihydronaphthalenes are also formed in less than 30% yield.



(1) G. D. Sargent, C. M. Tatum, Jr., and S. M. Kastner, *J. Amer. Chem. Soc.*, **94**, 7174 (1972).

(2) For a recent, comprehensive, authoritative review of carbene chemistry, see W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

Scheme I



The principal components of the volatile product mixture are methane and ethylene. While methane might result from simple, step-wise reduction of the methylene halide, the formation of ethylene in high yield requires that a more complicated mechanism be operative. Simple dimerization of methylene seems an unlikely route to ethylene, since it is hardly credible that a process second order in methylene (dimerization) could occur to the virtual exclusion of methylene addition to cyclohexene, a process first order in methylene and first order in cyclohexene, which is present in great excess.

In the absence of any compelling reason to expect that the methylene halides should behave differently from their alkyl substituted analogs on treatment with **1**, one is forced to conclude that the carbene (carbenoid) generated from the methylene halides is trapped by some process substantially more efficient than addition to cyclohexene. Control experiments established that neither DME nor naphthalene functions as an efficient methylene trap in the presence of excess cyclohexene. We conclude, therefore, that sodium naphthalene must be the reagent which inhibits methylene addition to cyclohexene. Since alkyl naphthalenes and dehydronaphthalenes represent only a minor fraction of the methylene halide derived products, we suggest that the principal mechanism by which methylene is trapped involves electron transfer to generate the methylene radical anion. An abbreviated outline of a plausible mechanism which incorporates this hypothesis is outlined in Scheme I.

If Scheme I is to account accurately for the low yield of norcaradiene from the reaction of **1** with a methylene halide in the presence of cyclohexene, two conditions must pertain: (1) the rate of reaction 2 must be much greater than that of reaction 1 and (2) the methylene radical anion must not itself readily add to cyclohexene. Since *tert*-butylmethyl carbene [(CH₃)₃CCCH₂] is reduced by **1** to the corresponding carbene radical anion [(CH₃)₃CCCH₂]⁻ at a rate competitive with that of *intramolecular* C-H insertion,¹ one might well expect that similar reduction of the methylene radical anion should be highly competitive with *intermolecular* addition of methylene to cyclohexene. Evidence that the methylene radical anion (3) should eschew addition to cyclohexene is found in the observed failure of amino radicals in general, and the simplest amino radical $\dot{\text{N}}\text{H}_2$, which is isoelectronic with **3**, in particular, to add to cyclohexene.³

The reactions of the methylene radical anion postulated in Scheme I find precedent in the behavior of alkyl anions (or sodium alkyls) generated by reaction of **1** with simple alkyl halides⁴ and support in the relative yields of methane and ethylene actually formed from the methylene halides (Table I). For ethylene to be

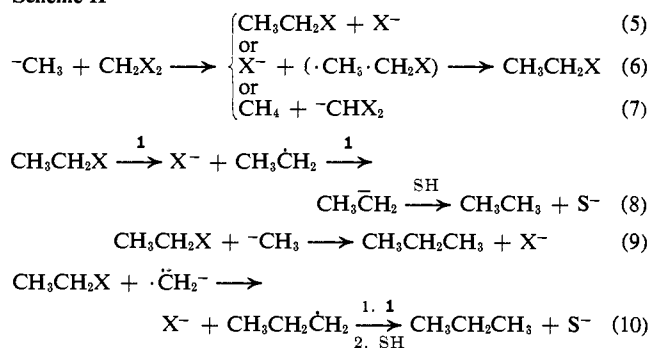
Table I. Relative Yields of Low Molecular Weight Hydrocarbons Generated by Reaction of Sodium Naphthalene with Methylene Halides

Product	Reactant		
	CH ₂ Cl ₂	CH ₂ Br ₂	CH ₂ I ₂
CH ₄	34	28	23
C ₂ H ₆	5	7	10
C ₂ H ₄	59	61	61
C ₃ H ₈	2	4	6

formed in greater yield than methane, these two products must be formed either by two completely independent routes or a common intermediate must at some stage be partitioned between competitive modes of reaction, one of which must lead to the formation of ethylene to the exclusion of methane. The first of these alternatives appears totally unreasonable; the second is incorporated in Scheme I.

Ethane and propane are also formed from the reaction of **1** with the methylene halides, though in diminished yield relative to ethylene and methane (Table I). Ethane and propane are both rationally derived from ethyl halide which, in turn, is most simply rationalized as the product of the reaction of methyl anion with the methylene halide (Scheme II). Since

Scheme II



(3) Y. Ogata, Y. Izawa, and H. Tomioka, *Tetrahedron*, **23**, 1509 (1967); W. P. Hoss, Ph.D. Thesis, University of Nebraska, 1971.

(4) A review: J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

the methylene halide is also a potential proton source, one might well expect formation of methane and ethyl halide, and hence ethane and propane, to be competitive. In theory, formation of ethyl halide might result either from direct displacement (eq 5) or from dissociative electron transfer followed by radical coupling (eq 6). Either mechanism predicts the following reactivity order for ethyl halide formation: $\text{CH}_2\text{I}_2 > \text{CH}_2\text{Br}_2 > \text{CH}_2\text{Cl}_2$.⁵ The ease of proton transfer from methylene halide to methyl anion (eq 7) should not, however, be particularly halogen sensitive.⁶ The halogen dependence of the relative yields of methane, ethane, and propane observed experimentally (Table I) is thus wholly consistent with the mechanism proposed in Scheme II.

The constant relative yield of ethylene generated by the three methylene halides requires that the competition between carbon-carbon bond formation and proton abstraction which characterizes the methyl anion-methylene halide interaction be inoperative during methylene radical anion-methylene halide encounters. Either this reaction does not contribute substantially to ethylene formation or, as seems more likely, the methylene radical anion is simply a far more potent reducing agent (or nucleophile) than it is a base so that each methylene radical anion-methylene halide encounter leads to carbon-carbon bond formation either by dissociative electron transfer and coupling or by direct displacement (eq 3, Scheme I). To the extent that methylene radical anion dimerization (eq 4) represents the source of ethylene, one would, of course, expect the relative yield of ethylene to be insensitive to the nature of the halide employed. The crucial step in this mechanistic postulate is the initial dimerization.⁷ Since the reduction potential of ethylene is more negative than that of naphthalene, the two subsequent one-electron transfer reactions to naphthalene might well be sufficiently rapid with respect to proton abstraction by the dianion to obviate that species as a prime source of ethane.

In summary, we believe the results reported here support our suggestion¹ that the carbenes or carbenoids generated by reaction of sodium naphthalene with alkyl geminal dihalides can be further reduced to carbene radical anions at rates competitive with those of typical carbene (carbenoid) reactions—in this case, intermolecular addition to an olefinic double bond. In addition they provide the first example(s), other than proton abstraction, of chemistry characteristic of a carbene radical anion, *i.e.*, formal nucleophilic displacement and/or dimerization to a dianion. Finally they

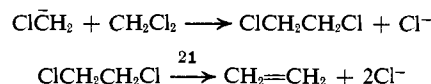
(5) The polarographic half-wave potentials (*vs.* NCE) for CH_2Cl_2 , CH_2Br_2 , and CH_2I_2 are, respectively, -2.23 , -1.48 , and -1.12 V [M. V. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949)]; the relative leaving group abilities of the halides for displacement at saturated carbon are $\text{I} > \text{Br} > \text{Cl}$ [see, *e.g.*, E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 80-81, and references therein cited].

(6) No data are available for the $\text{p}K_a$'s of the methylene halides, but by analogy to the behavior of the haloforms [J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957)] one would expect the kinetic acidities of CH_2I_2 and CH_2Br_2 to be nearly identical and only slightly greater than that of CH_2Cl_2 .

(7) Although this mechanistic postulate intrigued us from the moment the data of Table I were obtained, we were too timid to suggest formation of the ethylene dianion in the original version of this communication. We are emboldened to present this postulate here by its independent suggestion by a referee, who notes "a reader...repulsed by piling up all that negative charge...should [keep] in mind that ion aggregation factors can overcome most of that."

suggest that in reaction with a substrate which can function both as a proton source and as a substrate for nucleophilic displacement (or dissociative electron transfer), the methylene radical anion favors nucleophilic attack over proton abstraction to a greater extent than does the methyl anion (methyl sodium).

Finally, we must admit the obvious, namely, that we cannot conclusively eliminate all alternatives to the interpretation presented here. In particular, we cannot with certainty exclude the possibility that ethylene formation results from the sequence



The constancy in the relative yield of ethylene from the three methylene halides is difficult to rationalize by such a hypothesis, however, and, in general, the totality of the data, for reasons too involved to elaborate here, in our opinion, militates against the plausible alternatives to the carbene radical anion postulate.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research.

(8) National Science Foundation Undergraduate Research Participant.

G. Dann Sargent,* Charles M. Tatum, Jr.⁸
Richard P. Scott⁸

Department of Chemistry, Amherst College
Amherst, Massachusetts 01002

Received June 7, 1973

Relationship of Nitrogen Lone Pair Interactions to Thermodynamic Parameters Associated with Amine Basicities

Sir:

The interaction of orbitals through space and through bonds has been a topic of increasing interest in recent years,¹ stimulated largely by the development of photoelectron spectroscopy (PES).² Hoffmann¹ considers the extent of interaction to be measured by the magnitude of the one-electron energy level splitting after interaction, compared to that splitting in the (theoretical) absence of such interaction or in a model compound where that interaction is absent. While PES provides a direct measure of one-electron orbital energies,^{2,3} there are other chemical properties which may provide a measure of such interactions. We wish to report the determination of the gas-phase basicities (proton affinities) of I and II in the absence of solvation phenomena using the techniques of ion cyclotron resonance spectroscopy⁴ and delineate the relationship between nitrogen lone pair interactions and thermodynamic parameters associated with amine basicity.

Gas-phase and solution basicities of I and II along

(1) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, New York, N. Y., 1970.

(3) This assumes that Koopmans' theorem is valid.

(4) For a recent review, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). Trapped ion techniques used in the present study are described in T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).