period. Stirring was continued for 30 min. at 5°, and the reaction mixture was poured onto 1 l. of crushed ice. The mixture was extracted with ether, and the combined extracts were dried over potassium carbonate. Distillation gave, after removal of ether and benzene and a small forerun, 36.3 g. (64%) of a mixture of two ketones, b.p. 136–137°, n^{20}_{D} 1.4060. The two components were shown by gas chromatography to be present in about a 3:2 ratio. The two expected rearrangement products are 3-methyl-2-hexanone and 2-methyl-3-hexanone, and the former should predominate.

Anal. Calcd. for $C_7H_{14}O$: C, 73.8; H, 12.3. Found: C, 73.78; H, 12.33.

Rearrangement of 1-Propylcyclohexanecarboxaldehyde.—1-Propylcyclohexanecarboxaldehyde (102 g., 0.66 mole), was added over a 10-min. period to a stirred mixture of 300 ml. of benzene and 300 ml. of concentrated sulfuric acid at 5–10°. Stirring was continued for 30 min. at 5–6°, and the mixture was poured onto cracked ice and treated as in the preceding example. The sole ketonic product was 58.5 g (57%) of 1-cyclohexyl-1-butanone, b.p. 92.5–93.5° (13.5 mm.), n^{20}_{D} 1.4532, which was shown by gas chromatography to be homogeneous. The product gave a 2,4-dinitrophenylhydrazone, m.p. 114.5–115.5°, and a semicarbazone, m.p. 154–155°. Reported[12] values are: for 1-cyclohexyl-1-butanone, b.p. 79° (6 mm.), n^{20}_{D} 1.4531; 2,4-dinitrophenylhydrazone, m.p. 114°; semicarbazone, m.p. 155°.

Acknowledgment.—The author wishes to express his appreciation for the technical assistance of Joyce Gillenwater, Herman S. Pridgen and Mrs. Billie C. Renfro. The procedure for the hydrogenation of the terminal double bond was provided by James C. Martin, who first carried out this reaction.

[12] H. H. Morris and M. L. Lusth, THIS JOURNAL, **76**, 1237 (1954).

KINGSPORT, TENN.

[CONTRIBUTION FROM COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Methylene, CH$_2$. Stereospecific Reaction with *cis-* and *trans*-2-Butene

BY ROBERT C. WOODWORTH[1] AND PHILIP S. SKELL

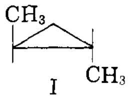
RECEIVED DECEMBER 31, 1958

Methylene from the photolysis of diazomethane exhibits stereospecific addition to the 2-butenes both in the formation of the 1,2-dimethylcyclopropanes and the 2-pentenes. Not only do these facts help confirm the existence of methylene as an intermediate species, but they also show that photolytically-produced methylene exists in a singlet, rather than a triplet, state both in the gas phase and in solution.

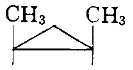
Introduction

Much work appearing in recent literature attests to the existence of intermediate reactive species, called carbenes or methylenes, consisting of carbon atoms with two singly covalently-bonded substituents and two non-bonded electrons.[2] The electrophilic, non-free radical character of some carbenes has been established by relative rate[3-5] and stereospecificity[2c,6-9] studies of their additions to various olefins. These additions appear to be of the three-center, rather than free-radical, type.[4] As a consequence of these findings and the fact that reactions involving a change in multiplicity are slow,[10] the two non-bonded electrons of a carbene must be in a singlet state at the time of the addition to the two paired π-electrons of the olefin. The quantum state of the carbene molecule at the point of its creation remained open to question, however. If the carbene was in a triplet state when created, the inhomogeneous magnetic field provided by high-atomic weight covalently-bonded substituents, such as halogens, could have catalyzed the interconversion of the triplet to a singlet state.[11,12]

Therefore, we have studied the addition of methylene itself to the 2-butenes, feeling that the presence of two hydrogen atoms, rather than larger substituents, would minimize the possibilities of interconversion. Our major criterion is the stereospecificity of addition or its lack, the former indicating a three-center addition and thereby a singlet state for the carbene.[2c,9] The stereospecific addition of methylene would thus yield *trans*-1,2-dimethylcyclopropane (I) from *trans*-2-butene, and *cis*-1,2-dimethylcyclopropane (II) from *cis*-2-butene.



I



II

This type of system provides then a unique contradiction to the generally acceptable principle that knowledge of the structure of reaction products is a poor guide for distinguishing between structures which differ in electron arrangement.

A preliminary report concerning this work[2c] has been criticized by Kistiakowsky and Sauer on the basis that we had not considered the efficiency of this reaction.[13] A low relative efficiency would make interconversion of a triplet to a singlet state

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[1] National Science Foundation pre-doctoral fellow. This manuscript is taken from a portion of Robert C. Woodworth's thesis for the Ph.D. degree, August, 1956.

[2] For extensive references see: (a) J. Hine and F. P. Prosser, THIS JOURNAL, **80**, 4282 (1958), XIII in a series entitled "Methylene Derivatives as Intermediates in Polar Reactions"; (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496, 6577 (1956); (d) W. von Doering, R. G. Buttery, R. G. Laughlin and N. Chanduri, *ibid.*, **78**, 3224 (1956); (e) W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 2688 (1954).

[3] P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1958).

[4] P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956).

[5] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[6] R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

[7] W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

[8] H. M. Frey, *ibid.*, **80**, 5005 (1958).

[9] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

[10] For references see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 61, 107, 198, 326.

[11] D. S. McClure, N. W. Blake and P. L. Hanst, *J. Chem. Phys.*, **22**, 255 (1954); D. S. McClure, *ibid.*, **17**, 908 (1949); M. Kasha, *ibid.*, **20**, 71 (1952); *Disc. Faraday Soc.*, **9**, 14 (1950).

[12] E. Gelles and K. S. Pitzer, THIS JOURNAL, **77**, 1974 (1955).

[13] G. B. Kistiakowsky and K. Sauer, *ibid.*, **78**, 5699 (1956); G. B. Kistiakowsky and P. H. Kydd, *ibid.*, **79**, 4825 (1957).

more probable during the many ineffective collisions a methylene molecule might undergo before adding to an olefin molecule. In addition to the criticism, however, was a report of studies of photolyses of ketene, which indicated that the reaction of methylene is indeed highly efficient. The cogency of our arguments is thereby supported.

Experimental

Materials.—The isomeric 2-butenes (*trans*, low boiling; *cis*, high boiling), obtained from Phillips Petroleum Co., were Pure Grade (99 mole-% minimum purity). Nitrosomethylurea was prepared by the method of reference 14, a yield of 119 g. (74%) of dry product being obtained from 46 g. (1.5 moles) of methylamine.

Analyses.—The working bases for comparison of products obtained from the reactions studied were infrared spectra derived from a Perkin–Elmer model 21 spectrophotometer equipped with NaCl optics. Unreacted *cis*- and *trans*-2-butenes were identified by comparison of their spectra with those of the pure olefins. The presence or absence of all C_5-monoölefins in the reaction mixtures from photolyses of diazomethane with the 2-butenes was determined by comparing the infrared spectra of distilled fractions with the following infrared absorption spectra, American Petroleum Institute Research Project 44.

Olefin	Infrared spectrum number
1-Pentene	356
cis-2-Pentene	357
trans-2-Pentene	358
2-Methyl-1-butene	359
3-Methyl-1-butene	360
2-Methyl-2-butene	361

All spectra were taken of distilled fractions in the gas phase at a pressure of 75 mm. in a 10.0-cm. cell fitted with NaCl optics. The identity of the *cis*- and *trans*-1,2-dimethylcyclopropanes was established by comparing the infrared spectra of our distilled, neat liquid hydrocarbons in a 0.111-mm. cell with infrared spectra of the known, neat liquid 1,2-dimethylcyclopropanes in a 0.112-mm. cell, from 7.5 to 14.5 μ.[15]

Procedure.—All apparatus was mounted in an efficient fume hood during the preparation and making of a run. During an experiment the window was raised only enough to allow the experimenter access to the equipment.

Vapor-phase Reactions.—The reaction chamber for vapor-phase reactions was a 12-l. Pyrex bulb fitted with three stopcocks. One stopcock was connected to a manometer; the second was connected through a train of a spiral trap in a Dry Ice–acetone-bath and two U-traps in liquid nitrogen to a vacuum pump; and the third was attached to a line which ran through a potassium hydroxide pellet drying tube to the diazomethane generator. The diazomethane generator consisted of a 300-ml. round-bottomed flask equipped with two outlets, one to the reaction bulb *via* the drying tube and the other to a Bunsen valve for relieving any sudden surges in gas pressure.

After the 12-l. Pyrex bulb had been evacuated to a pressure of 1-mm., an appropriate amount of 50% aqueous potassium hydroxide was placed in the generator and cooled in a freezing carbon tetrachloride-bath to −10° or lower. Liquid olefin was poured into the generator followed by the desired amount of nitrosomethylurea. The generator was closed, then transferred to an ice-bath and shaken. If the reaction became vigorous, causing the reaction mixture to foam and gas to exit from the Bunsen valve, the generator was quickly returned to the freezing carbon tetrachloride bath where the reaction soon subsided.

Upon completion of reaction in the generator the olefin–diazomethane mixture was allowed to vaporize through the drying tube into the evacuated bulb to pressures equal to or less than atmospheric pressure. The bulb was then irradiated with a General Electric A-H6 high-pressure mercury-arc lamp (1000-watt) in a quartz jacket placed about two inches from the side of the bulb for a period sufficient to dissipate the yellow color of diazomethane.

The bulb was re-evacuated to 1 mm., most of the product condensing in the spiral trap and unreacted olefin condensing in the U-traps. The U-traps were removed from the line and their contents melted and returned to the generator for recycling.

After the final run of a series, the bulb was evacuated to 1 mm. and the contents of all three traps were combined and distilled through a 61-cm. by 8-mm. Podbielniak Mini-Cal column packed with Heli-Grid. While the unreacted 2-butene was distilling, the reflux condenser was maintained at 1°, and the butene fraction was collected in a Dry Ice-cooled trap at the column head. After all the butene had distilled and the reflux temperature had risen to 25–30°, the reflux condenser was cooled with tap water, 12–15°.

During all reactions a small amount of viscous liquid condensed on the inside of the bulb. This liquid could not be vaporized from the bulb by pumping but was soluble in acetone. It darkened rapidly in air and had a foul odor.

Liquid-phase Reactions.—Generation of diazomethane was carried out as described above. The olefin–diazomethane mixture was allowed to vaporize through the potassium hydroxide drying tube into a 100-ml., round-bottomed Pyrex flask fitted with a sidearm for introduction of reactants and a Dry Ice reflux condenser connected through a potassium hydroxide drying tube to a wet test meter. The flask was irradiated with a Pyrex-jacketed General Electric A-H6 high-pressure mercury-arc lamp placed about 1 cm. under the flask for a period sufficient to decolorize the diazomethane and to produce approximately the theoretical amount of nitrogen gas. The reaction mixture was then returned to the generator for recycling.

After completion of the series, the entire reaction mixture was distilled as described above. During all reactions a small amount of viscous, light-yellow, semi-solid material precipitated. It darkened rapidly in air and had a foul odor.

Vapor-phase Reaction of *trans*-2-Butene with Diazomethane.—The series of runs for *trans*-2-butene involved 38.2 g. (0.681 mole) of olefin, 120 ml. of 50% potassium hydroxide and 40.1 g. (0.390 mole) of nitrosomethylurea. Irradiation time totaled 250 min. An infrared spectrum of the unreacted olefin was indistinguishable from that of the starting olefin. Distillation of the reaction mixture showed that approximately equal quantities (0.5 g.) of *trans*-1,2-dimethylcyclopropane and *trans*-2-pentene and a trace of 2-methyl-2-butene were recovered. About 0.5 g. of material boiling 37–95° was not identified.

Vapor-phase Reaction of *cis*-2-Butene with Diazomethane.—The series of runs for *cis*-2-butene involved 59.7 g. (1.06 moles) of olefin, 180 ml. of 50% potassium hydroxide and 57 g. (0.55 mole) of nitrosomethylurea. Irradiation time totaled 395 min. An infrared spectrum of the unreacted olefin was indistinguishable from that of the starting olefin. Distillation of the reaction mixture and infrared analysis showed that approximately equal quantities (2.3 g.) of *cis*-1,2-dimethylcyclopropane and *cis*-2-pentene and smaller amounts of 2-methyl-2-butene (0.5 g.) and *trans*-1,2-dimethylcyclopropane (0.05 g.) were recovered. There was a non-distilled residue of 1.6 g.

Liquid-phase Reaction of *trans*-2-Butene with Diazomethane.—The series of runs for *trans*-2-butene involved 30.0 g. (0.540 mole) of olefin, 120 ml. of 50% potassium hydroxide and 40 g. (0.39 mole) of nitrosomethylurea. Irradiation of the olefin–diazomethane mixture for 170 min. caused the evolution of 7.9 l. of nitrogen. An infrared spectrum of the unreacted olefin was indistinguishable from that of the starting olefin. Distillation of the reaction mixture and infrared analysis showed that approximately 2.1 g. of *trans*-1,2-dimethylcyclopropane, 1.2 g. of *trans*-2-pentene and 0.03 g. of 2-methyl-2-butene were recovered. There was a non-distilled residue of 2.9 g.

Liquid-phase Reaction of *cis*-2-Butene with Diazomethane.—This run involved 27.4 g. (0.489 mole) of *cis*-2-butene, 120 ml. of 50% potassium hydroxide and 38 g. (0.37 mole) of nitrosomethylurea. Irradiation of the olefin–diazomethane mixture for 70 min. caused the evolution of 6.7 l. of nitrogen. An infrared spectrum of the unreacted olefin was indistinguishable from that of the starting olefin. Distillation of the reaction mixture and infrared analysis showed that approximately equal quantities (1.5 g.) of *cis*-1,2-di-

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(14) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 461.

(15) We are indebted to Professor H. Pines of Northwestern University for supplying the infrared spectra of the isomeric 1,2-dimethylcyclopropanes in liquid phase for comparison.

methylcyclopropane and *cis*-2-pentene, smaller amounts of 2-methyl-2-butene (0.14 g.) and 2-methyl-1-butene (0.03 g.), and a trace of *trans*-1,2-dimethylcyclopropane were recovered. There was a non-distilled residue of 3.6 g.

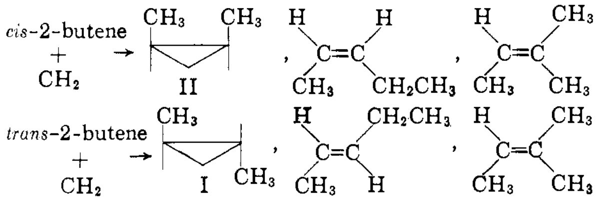
Chemical Analysis of Distilled *cis*-1,2-Dimethylcyclopropane and *cis*-2-Pentene Mixtures and Isolation of Pure *cis*-1,2-Dimethylcyclopropane.—Various fractions, boiling 31.2–35.3°, of products from reactions of *cis*-2-butene with diazomethane were combined giving a total of 2.91 g. (0.0415 mole) of C_5H_{10} hydrocarbons. This mixture was placed in an ice–salt–water-bath and titrated with neat liquid bromine over a period of 45 min. The end-point was assumed when the bromine color persisted for 10 sec. and evolution of hydrogen bromide commenced. The titration required 1.130 ml. of 3.47 g. (0.0218 mole) of bromine at room temperature (32°, d_{32} 3.119 g./ml.). The total weight increase of the titration flask was 3.48 g. The entire titration mixture was distilled through a 10-cm. by 8-mm. tube, yielding 0.72 g. of material, b.p. 37.0° (736 mm.), whose infrared spectrum was indistinguishable from that of pure *cis*-1,2-dimethylcyclopropane, and 3.4 g. of material, b.p. 65–67.8° (16 mm.), n^{25}_{D} 1.5061.

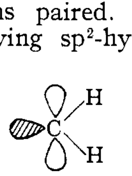
Infrared Spectra of the 1,2-Dimethylcyclopropanes.—The following liquid phase spectra were recorded neat in 0.111-mm. thicknesses: *trans*-1,2-dimethylcyclopropane: 2.27-(vw), 2.32(w), 2.35(mw), 2.43(w), 2.52(vw), 3.30(s), 3.34–3.50(vs), 3.65(m), 4.95(w), 6.17(w), 6.82(vs), 6.91(vs), 7.19(s), 7.43(ms), 8.55(ms), 9.13(ms), 9.30(ms), 9.66(s), 9.86(s), 10.23(m), 10.93(m), 11.40(m), 11.87(s), 13.07(s), 13.41(s); *cis*-1,2-dimethylcyclopropane: 2.32(w), 2.35(mw), 2.38(w), 2.43(w), 2.48(vw), 3.29(s), 3.35–3.52(vs), 3.62-(mw), 3.68(m), 4.94(w), 6.07(w), 6.56(w), 6.86(vs), 6.93(vs), 7.24(s), 7.62(ms), 8.23(vw), 8.52(mw), 9.07(m), 9.31(s), 9.84(vs), 10.29(s), 11.51(s), 12.78(m), 13.08(m).

Gas phase spectra were obtained in 10-cm. cells with pure olefins at approximately 70 mm. partial pressure: *trans*-1,2-dimethylcyclopropane: 3.21(w), 3.28(ms), 3.36(s), 3.42(vs), 3.50(s), 3.66(w), 6.82(s), 6.90(ms), 7.17(mw), 7.21(m), 7.55(mw), 7.59(mw), 7.64(mw), 8.51(w), 9.24-(mw), 9.32(mw), 9.72(m), 9.79(ms), 9.87(m), 10.18(mw), 10.26(m), 10.37(mw), 11.17(m), 11.55(ms), 12.95(mw), 13.06(m); *cis*-1, 2-dimethylcyclopropane: 3.28(ms), 3.35-(s), 3.42(vs), 3.48(s), 3.63(w), 6.78(ms), 6.88(s), 7.16(m), 7.35(w), 7.40(mw), 7.46(w), 8.52(mw), 9.18(mw), 9.27(mw), 9.53(mw), 9.61(m), 9.71(m), 9.82(m), 9.90(mw), 10.85(w), 10.97(w), 11.41(w), 11.85(m), 12.85(mw), 13.02(m), 13.19(m), 13.37(ms), 13.55(m).

Discussion

Methylene does indeed undergo *cis*-stereospecific addition, *trans*-2-butene yielding I and *cis*-2-butene yielding II, both in gas- and liquid-phase photolyses with diazomethane. The conclusion follows that the methylene molecules produced during these reactions existed in a singlet state (not necessarily the ground state[16]) with their non-bonded electrons paired. Structure III, a planar molecule having sp^2-hybridization and a vacant *p*-orbital, is therefore suggested for methylene. This structure assignment is consistent with those proposed on the basis of quantum mechanical calculations.[17]

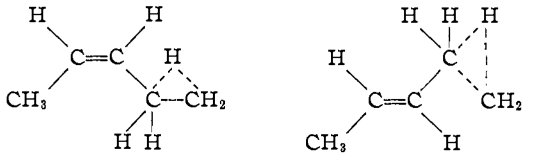




III

In addition to the dimethylcyclopropanes other C_5H_{10} hydrocarbons were produced as follows: *trans*-2-butene yielded *trans*-2-pentene in amounts roughly equal to those of I; *cis*-2-butene yielded *cis*-2-pentene in amounts roughly equal to those of II; and both 2-butenes yielded smaller amounts of 2-methyl-2-butene. Traces of 2-methyl-1-butene and *trans*-1,2-dimethylcyclopropane from the *cis*-2-butene reactions are not inconsistent with the mole purity of the starting olefin.

The stereospecific formation of the 2-pentenes suggests that the conversions of C–H to C–CH_3 bonds[2d,18] are substitution reactions of the 2-butenes, in which CH_2 is inserted into the C–H bond. Possible intermediates in this *insertion substitution* are pictured below. The intermediates for these substitution reactions are similar to that proposed



for the methylene plus hydrogen reaction.[19] The 2-methyl-2-butene may be produced by substitution on the vinylic C–H bond, or alternatively the dimethylcyclopropanes, which are undoubtedly produced in vibrationally excited states,[13,16] may undergo thermal rearrangement to produce 2-methyl-2-butene and 2-methyl-1-butene.

It is conceivable that the 2-pentenes and 2-methyl-2-butene result from a methylene molecule abstracting a hydrogen atom from a 2-butene molecule, producing methyl and crotyl radicals. Chain processes are also conceivable. The stereospecific formation of *cis*-2-pentene from *cis*-2-butene and *trans*-2-pentene from *trans*-2-butene does not preclude a radical mechanism because the crotyl radical may be resonance stabilized with no shift in atomic nuclei, thereby maintaining the geometric configuration of the double bond.

$$:CH_2 + CH_3CH{=}CHCH_3 \longrightarrow \cdot CH_3 + \cdot CH_2CH{=}CHCH_3 \quad (1)$$

$$\cdot CH_3 + \cdot CH_2CH{=}CHCH_3 \longrightarrow CH_3CH_2CH{=}CHCH_3 \quad (2)$$

However, there are several considerations which argue against the production of the 2-pentenes and 2-methyl-2-butene *via* a radical mechanism. The large amount of light necessary to decompose the diazomethane during the course of these reactions is not consistent with a high-quantum yield, and thus excludes radical-chain mechanisms. Also,

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[16] H. M. Frey and G. B. Kistiakowsky, THIS JOURNAL, **79**, 6373 (1957).

[17] J. Lennard-Jones and J. A. Pople, *Disc. Faraday Soc.*, **10**, 9 (1951); K. J. Laidler and E. J. Casey, *J. Chem. Phys.*, **17**, 213 (1949); H. H. Voge, *ibid.*, **4**, 581 (1936); J. Lennard-Jones, *Trans. Faraday Soc.*, **30**, 70 (1934).

[18] A. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

[19] J. Chanmugam and M. Burton, THIS JOURNAL, **78**, 509 (1956); see also for earlier references to discussions of this mechanism.

Frey and Kistiakowsky[16] have demonstrated that methyl radicals are not responsible for the C–H substitutions of CH_2 by demonstrating that free oxygen does not affect the course of this type of substitution reaction.

University Park, Penna.

[Contribution from the School of Chemistry of the University of Minnesota]

The Reaction of Bis-(substituted-mercapto)-ethylenes with *n*-Butyllithium[1]

By William E. Parham, Robert F. Motter[2] and Gwendolyn L. O. Mayo

Received January 2, 1959

n-Butyllithium reacts with bis-(substituted-mercapto)-ethylenes by elimination of mercaptide to give substituted mercaptoacetylenes: $RSCH{=}CHSR + C_4H_9Li \longrightarrow RSLi + HC{\equiv}CSR$. A series of symmetrical and unsymmetrical vinyl sulfides and vinyl ethers of this type has been prepared and the reaction of these compounds with *n*-butyllithium has been studied. The reaction has been found to be quite general for the synthesis of alkyl or arylmercaptoacetylenes, with little preference in elimination of normal alkyl or aromatic mercaptide. The reaction is, however, subject to steric and electrical effects, and the products of reaction are consistent with a β-elimination mechanism, but inconsistent with an α-elimination mechanism.

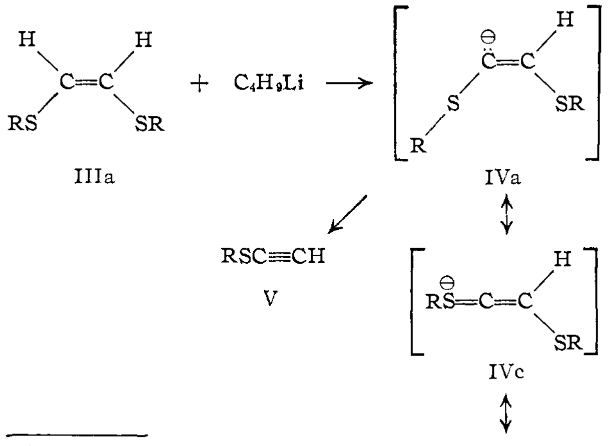
Parham and Stright[3] recently described a new synthesis of phenylmercaptoacetylene (II) by reaction of *cis*- or *trans*-1,2-bis-(phenylmercapto)-ethylene (I) with butyllithium.

$$\underset{\text{I}}{C_6H_5SCH{=}CHSC_6H_5} + C_4H_9Li \longrightarrow \underset{\text{II}}{C_6H_5SC{\equiv}CH} + C_6H_5SLi$$

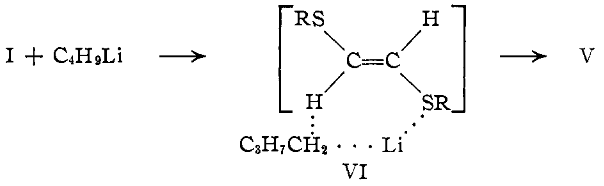
The results described in this report summarize further studies which were designed: (a) to define the scope of the reaction, and (b) to furnish additional information concerning the reaction sequence by which the products are formed.

Elimination reactions which are formally analogous to the one described above are well known, and three general mechanisms can be formulated: β-elimination[4] (equation A), cyclic transition state[5] (equation B) and α-elimination

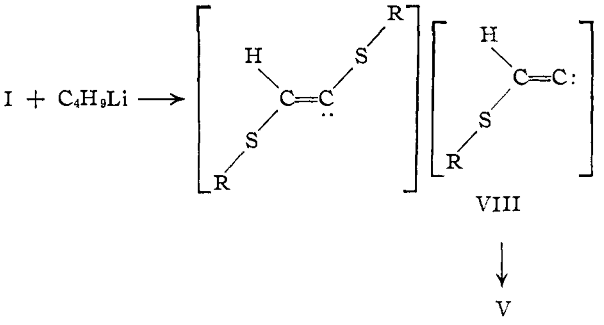
A. (β-elimination mechanism)



B. (cyclic transition state)



C. (α-elimination)



Our initial attempts to elucidate the course of this reaction by kinetic studies[6] were unsuccessful. *cis*- and *trans*-bis-(phenylmercapto)ethylene were prepared, and a rapid spectrophotometric method for the quantitative determination of lithium thiophenolate was developed. However, the rapid rate at which both *cis*- and *trans*-I react (reaction complete after one minute) under the conditions employed (25°, 4.9×10^{-5} molar in I, 1.5×10^{-3} molar in butyllithium) has precluded obtaining reliable kinetic data.

Definition of the scope of the elimination reaction, as well as further data concerning the

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[1] This work was supported by the Office of Ordnance Research, Contract No. DA-11-022-Ord-2616.

[2] From the Ph.D. thesis of Robert F. Motter, University of Minnesota, 1958.

[3] W. E. Parham and P. L. Stright, This Journal, **78**, 4783 (1956).

[4] *Cf.* (a) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951); (b) W. E. Truce, J. A. Simms and M. Bodakian, *ibid.*, **78**, 695 (1956).

[5] *Cf.* (a) S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955); (b) A. Bothner-By, *ibid.*, **77**, 2393; (c) R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).

[6] If the β-elimination mechanism obtains, without rapid isomerization of the intermediate ions (IVa $\rightleftarrows$ IVb $\rightleftarrows$ IVc), then one would expect *trans* elimination from the *cis* isomer IIIa, to be more rapid than *cis* elimination from the *trans* isomer IIIb. Similarly, for the cyclic transition state mechanism (equation B) one would expect elimination from the *trans* isomer IIIb (*via* VI) to be more favorable than from the *cis* isomer, in view of the more favored transition state possible for the former.[5c]