A Comparative Study of Some Reactions of Dimethylvinylidene and Dimethylmethylidene

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Dimethylvinylidene and dimethylmethylidene have been compared with respect to their addition reactions with styrenes and insertion reactions into several R-H bonds in aprotic solvents. The results show that dimethylvinylidene is much more reactive than dimethylmethylidene in addition reactions with styrenes under the conditions used. Attention is brought to sight of a possible alkyl substituent effect in the insertion of alkylvinylidenes into Si-H bonds. Relative rates for thermal conversion of 1-(2-methylprop-1-enylidene)-2-phenylcyclopropanes to 1-isopropylidene-2-methylene-3-phenylcyclopropanes were determined and used as additional support for a radical mechanism for the thermal rearrangement. An attempt to prepare 1-lithio-1-bromo-3-methyl-1,2-butadiene, a possible precursor to dimethylvinylidene carbene, was not successful. A useful method for preparing 1,2-dibromo-3-methyl-1,3-butadiene is reported.

Reactions which proceed by transfer of an unsaturated divalent carbon intermediate to various substrates have received much attention.[2] We have directed our attention to a study which would allow some comparisons to be made between the reactivities of dimethylvinylidene A[3] and dimethylmethylidene B.[3] Our aim was to compare the reactivities of A and B in aprotic media with regard to their addition reactions with styrenes and insertion reactions into C–H and metal–H bonds. In addition, we sought to generate and identify an organometallic intermediate which could be a precursor or directly responsible for reactions of A. The results of our studies are the subject of this paper.

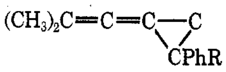
$(CH_3)_2C{=}C{=}C{:}$ **A** $(CH_3)_2C{=}C{:}$ **B**

Results and Discussion

Dimethylvinylidene (A) was generated from 1-bromo-3-methyl-1,2-butadiene (**1**)[4] and trapped with para-substituted styrenes (**2a–c**) to give 1-(2-methylprop-1-enylidene)-2-phenylcyclopropanes (**3a–c**)[5] in approximately 30% yields.

$(CH_3)_2C{=}C{=}CHBr$ **1**

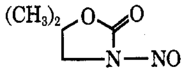
$CH_2{=}CHPhR$ **2a**, R = H; **b**, R = CH$_3$; **c**, R = Cl



3a, R = H
b, R = CH$_3$
c, R = Cl

Dimethylmethylidene (B) was obtained from 1,1-dibromo-2-methylpropene (**4**)[6] or 1-bromo-2-methylpropene (**5**)[7] and trapped with **2a–c** to give 2-phenylisopropylidenecyclopropanes (**7a–c**) in 11–20% yields. Compounds **7a–c** have been previously reported by the reaction of B generated from 5,5-dimethyl-*N*-nitroso-2-oxazolidone (**6**)[2d] with **2a–c**.

$(CH_3)_2C{=}CBr_2$ **4** $(CH_3)_2C{=}CHBr$ **5**



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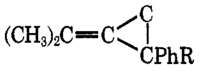

7a, R = H
b, R = CH$_3$
c, R = Cl

Relative rates of reaction of both A and B with styrenes were obtained by generating A from **1** or B from **4** and **5** in the presence of large excesses of the styrenes. The molar amounts of products from A were determined by mass spectrometry. The actual products analyzed were **8a–c**, which occur from rearrangement of **3a–c**, respectively[14] (see later discussion). The molar amounts of products from B were determined by vpc analysis. The results are given in Table I.

TABLE I

RELATIVE RATES OF ADDITION OF DIMETHYLVINYLIDENE AND DIMETHYLMETHYLIDENE TO STYRENES[a]

Styrene	$(CH_3)_2$-$C{=}C{=}C{:}$[b]	$(CH_3)_2$-$C{=}C{:}$[c]	$(CH_3)_2$-$C{=}C{:}$[d]	$(CH_3)_2$-$C{=}C{:}$[e]
p-H	1.0	1.0	1.0	1.0
p-CH$_3$	1.9	21	19	12
p-Cl	0.78	0.34	0.32	0.42
ρ[f]	−0.95	−4.3	−4.3	−3.4

[a] The approximate error is ±5%. [b] Generated from **1** (heterogeneous reaction). [c] Generated from **4** (homogeneous reaction). [d] Generated from **5** (heterogeneous reaction). [e] Data taken from ref 2d where B was generated from **6** (homogeneous reaction). [f] From Hammett equation using σ^+ values.

Certain points regarding the reactivities of A and B can be made from inspection of the data in Table I. The Hammett ρ values show that both A and B are reacting as electrophiles.[8] The ρ values for B indicate that B is sensitive to the substituents on the phenyl ring, whereas the low ρ value for A shows that the substituents influence the reactivity of A very little. The low electrophilic nature of A found here in *aprotic* media is in sharp contrast to the high polar character found for A in *protic* solvents.[9] Thus one should expect to

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(1) Address correspondence to this author.

(2) For some leading references see (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 67–75; (b) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969); (c) H. D. Hartzler, *J. Amer. Chem. Soc.*, **93**, 4527 (1971); (d) M. S. Newman and T. B. Patrick, *ibid.*, **91**, 6461 (1969); (e) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 7493 (1970).

(3) The chemistry of A has been described as carbene chemistry.[2c] The actual nature of A in *aprotic* media has been questioned by W. J. le Noble, Y. Tatsukani, and H. F. Morris, *ibid.*, **92**, 5681 (1970). The intermediate described by B is also questionable.[2d,e] We prefer to name both A and B in a manner which is noncommital as to the actual nature of the intermediate. Thus the names dimethylvinylidene and dimethylmethylidene do not infer carbene or organometallic character to the intermediates involved.

(4) D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Lett.*, 483 (1963).

(5) S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 5625 (1966).

(6) H. D. Hartzler, *J. Amer. Chem. Soc.*, **86**, 526 (1964).

(7) M. Tanabe and R. A. Walsh, *ibid.*, **85**, 3522 (1963).

(8) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(9) W. le Noble, *J. Amer. Chem. Soc.*, **87**, 2434 (1965).

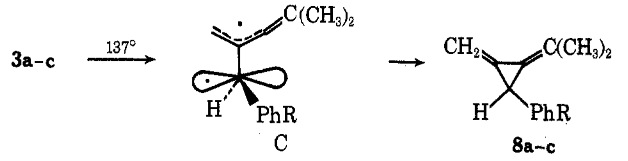
find the reactions of A to be influenced to a large extent by the nature of the solvent in which A is generated. The reactions of A and B reported by us are carried out in the same solvent system (styrene). The comparisons made between A and B are therefore valid.

The reactivity of B is nearly the same when B is generated homogeneously from **4** or heterogeneously from **5**. Although care should be exercised when comparing heterogeneous reactions, it appears as if the cation has little effect on the reactivity of B (Li^+ in **4**, K^+ in **5**). However, comparison of homogeneously generated B from both **4** and **6** where the cation is the same (Li^+) shows that the leaving group does affect the reactivity of B (Br^- in **4**, N_2 in **6**).[10]

There have been no reports of A being generated homogeneously in *aprotic* media. However, where comparisons of the reactivity of A from various precursors in heterogeneous media have been made, it is found that the cation and leaving group have little effect on the reactivity of A.[11,12]

For completeness in comparing the reactions of A and B we repeat here the already known facts that steric effects from substituents on A are small[12] whereas the substituents attached to B influence the reactions of B very markedly.[13]

We mentioned earlier in this paper that the analysis for products **3a–c** were carried out by mass spectrometry and that the products actually analyzed were 1-isopropylidene-2-methylene-3-phenylcyclopropanes (**8a–c**) which are formed by thermal rearrangements of **3a–c**.[14–16] This rearrangement was determined to occur quantitatively under the mass spectrometric conditions used. The mechanism of this rearrangement is considered to proceed through the nonplanar diradical C.[17,18] Having samples of **3a–c** on hand, we measured their rates of rearrangement to **8a–c** at 137°. (See Experimental Section.) The relative rates of rearrangement of **3a** (1.0), **3b** (1.1), and **3c** (1.3) give additional support for a radical mechanism.[19]



Reaction of A with triethylsilane (**9**) gave 1-(triethylsilyl)-3-methyl-1,2-butadiene (**10**) in 68% yield. Compound **10** underwent a thermal protrotropic rearrangement at 150–170° to give a 2:1 equilibrium mixture of **10** and 1-(triethylsilyl)-3-methyl-1-butyne (**11**).

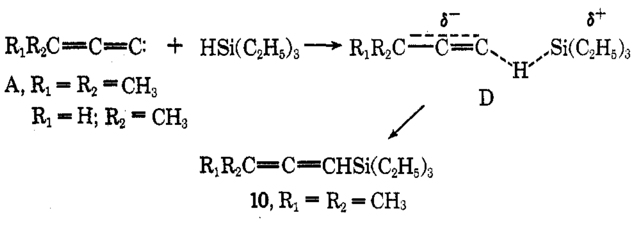
$$A + \underset{\mathbf{9}}{HSi(C_2H_5)_3} \longrightarrow \underset{\mathbf{10}}{(CH_3)_2C{=}C{=}CHSi(C_2H_5)_3} \xrightarrow{150-170°}$$

$$\mathbf{10}\ (67\%) + \underset{\mathbf{11}}{(CH_3)_2CHC{\equiv}CSi(C_2H_5)_3}\ (33\%)$$

The reaction of A with **9** is the first example of a dialkylvinylidene insertion reaction. A recent communication has reported the insertion of monoalkylvinylidene into Si–H and certain activated C–H bonds.[20] The fact that A inserts into **9** in 68% yield whereas methylvinylidene[20] inserts into **9** in 29% yield is of particular significance regarding vinylidene insertion reactions if these yields are a true reflection of the reactivity of the vinylidene involved. Insertion reactions of the highly electrophilic dichlorocarbene[21] into Si–H[22,23a] and C–H[23b,c] bonds have been postulated as proceeding by a concerted three-centered mechanism which may have some polar character.[23a,c]

Disubstituted vinylidenes have shown nearly the same reactivity regardless of their method of preparation.[10] The yield of Si–H insertion product from dimethylvinylidene (68%) compared with the yield of insertion product for methylvinylidene (29%)[20] suggests that the substituents cause vinylidenes to have *different* reactivity.

We offer here a suggestion as to reactivity differences which could occur in vinylidene insertion reactions. Reaction of the electrophilic vinylidene with a silicon hydride involve a transition state (D) which has dipolar character in which the negative portion of dipolar character in which the negative portion of the dipole is spread over the allylic system. Increasing alkyl substitution should lead to a decrease in the stability of the negatively charged part of the transition state.[24] Thus a difference in the reactivity of disubstituted alkyl vinylidenes *vs.* monosubstituted alkyl vinylidenes is to be expected. Our suggestion concerning the reactivity differences is based now on yield differences. We are presently testing the suggestion by obtaining more quantitative data. Similar dipolar mechanisms have been used to explain divalent carbon insertion into Si–H bonds.[12,23a]



We were unable to find products from insertion of A in C–H bonds of cumene or the Sn–H bond of tri-*n*-butyltin hydride. Insertion of methylidenes into Si–H bonds are well known.[12] Methylidenes are known to undergo intramolecular[25] C–H insertion and inter-

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[10] The general reaction sequence for generation of unsaturated divalent carbon is $RRC{=}CLK \xrightarrow{MN} RRC{=}CLM \xrightarrow{-ML} RRC{=}C\colon$, where L is the leaving group, K is a proton or halogen, M is the cation portion of a strong base N, and R is an alkyl or R-substituted vinyl group.

[11] D. S. Northington and W. M. Jones, *Tetrahedron Lett.*, 317 (1971).

[12] H. D. Hartzler, *J. Amer. Chem. Soc.*, **93**, 4527 (1971), and references cited therein.

[13] M. S. Newman and T. B. Patrick, *ibid.*, **92**, 4312 (1970).

[14] T. B. Patrick, E. C. Haynie, and W. J. Probst, *Tetrahedron Lett.*, 432 (1971).

[15] M. E. Hendrick, J. A. Hardie, and M. Jones, Jr., *J. Org. Chem.*, **36**, 3061 (1971).

[16] I. H. Sadler and J. A. C. Stewart, *J. Chem. Soc. D*, 1588 (1970).

[17] W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[18] J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971).

[19] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[20] J. C. Craig and C. D. Beard, *J. Chem. Soc. D*, 692 (1971).

[21] D. Seyferth, J. Y.-P. Mui, and J. M. Burtlich, *J. Amer. Chem. Soc.*, **89**, 4953 (1967).

[22] L. H. Sommer, L. A. Ulland, and A. Ritter, *ibid.*, **90**, 4486 (1968).

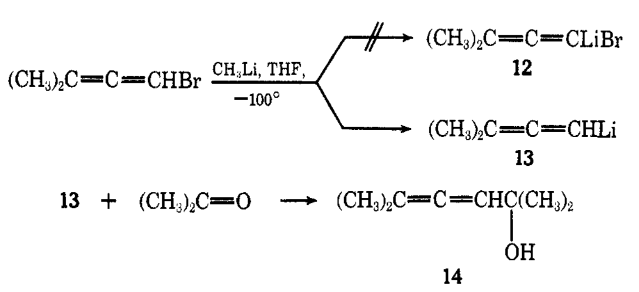
[23] (a) D. Seyferth, R. Damhauer, J. Y.-P. Mui, and T. F. Julia, *ibid.*, **90**, 2944 (1968); (b) D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburn, and C. J. Attridge, *J. Org. Chem.*, **35**, 1989 (1970); (c) D. Seyferth, U. A. Mai, and M. E. Gordon, *ibid.*, **35**, 1993 (1970).

[24] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 21.

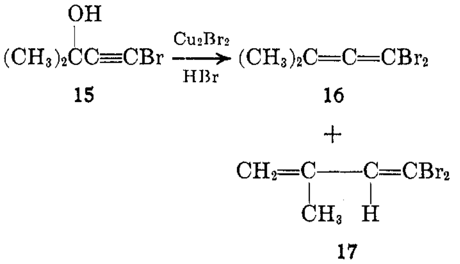
[25] K. L. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, **87**, 1142 (1965).

molecular C–H insertion when the methylidene is especially reactive.[2e]

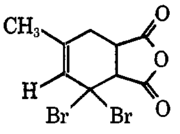
The extensive work reported by Kobrich[26] on the preparation and trapping of 1-lithio-1-haloethylene derivatives by reaction of vinyl halides with organolithium reagents in tetrahydrofuran (THF) at −100° prompted us to attempt the preparation and trapping of 1-lithio-1-bromo-3-methyl-1,2-butadiene (**12**) by treating **1** with methyllithium in THF at −100° followed by trapping with acetone. The only characterizable product from this attempt was 2-hydroxy-2,5-dimethyl-3,4-hexadiene (**14**), indicating that the reaction had proceeded by halogen–metal exchange to produce **13** which reacted with the acetone. No spectral evidence was found for the presence of a product resulting from **12**.



Efforts were made to synthesize 1,1-dibromo-3-methyl-1,2-butadiene (**16**), which could yield **12** on low-temperature treatment with methyllithium. The method used to prepare **16** was treatment of 1-bromo-3-methyl-1-butyne (**15**)[27] with Cu_2Br_2–HBr in a manner similar to that for the preparation of **1**.[4] The products from this reaction were a mixture of **16** (10%) and 1,1-dibromo-3-methyl-1,3-butadiene (**17**, 52%). On standing for seveal hours at room temperature, this mixture converted entirely to **17**. We were unable to isolate pure **16**.



The structure of **17** was based on its method of preparation, its Diels–Alder maleic anhydride adduct (**18**), and its nonidentity with isomeric 1,2-dibromo-3-methyl-1,3-butadiene (**19**), prepared by a reported procedure.[28]



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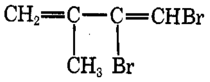

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Experimental Section[29]

Competitive Reactions with Styrenes. A. Dimethylvinylidene (A).—The method of Landor and Whiter[5] was used to generate dimethylvinylidene.

A stirred mixture containing 0.06 mol each of *p*-chlorostyrene, *p*-methylstyrene, and styrene and 0.006 mol of 1-bromo-3-methylbuta-1,2-diene (**1**) was cooled to −10° in a nitrogen atmosphere. *tert*-BuOK·*tert*-BuOH (0.006 mol) was added all at once. After stirring at −10° for 45 min, the mixture was filtered and analyzed directly by mass spectrometry to determine the molar amounts of **8a–c** present.

The mass spectra of **3a–c** were identical with their respective rearrangement products **8a–c**. Thus rearrangement occurred quantitatively under the mass spectrometer conditions used. Mass spectra[30] were recorded on mixtures containing known molar quantities of **8a–c** and the respective styrenes.

Intensities of the ions at *m/e* 155 (**8a**), 184 (**8b**), and 189 (**8c**) were found to serve as reliable measures of the molar quantities of products present. Values of molar quantities found by mass spectrometry were within 0.1% of the value expected from several standard mixtures.

Relative rates were obtained from the expression $k_2/k_1/k_0 = P_2/P_1/P_0$, where k's are the rate constants and P's are the molar amounts of products present. The values reported in Table I are an average of three runs.

B. Dimethylmethylidene (B) from 1,1-Dibromo-3-methylpropene (4).—To a stirred mixture of 0.1 mol of *p*-chlorostyrene (or *p*-methylstyrene), 0.1 mol of styrene, and 0.01 mol of **4**[6] (bp 154–156°) at −40° under nitrogen was added 10 ml (0.01 mol) of 1.0 *N* ethereal methyllithium. The mixture was stirred for 1 hr and then poured into water. The organic products were extracted into ether, washed with saturated sodium chloride solution, and dried by filtration through anhydrous magnesium sulfate. Most of the ether was removed by distillation and the remaining liquid was analyzed by vpc. A 5 ft × 0.25 in. column of 20% FFAP on Chromosorb W, 60–80 mesh at 150° and nitrogen flow of 60 ml/min, was used for separation on an Aerograph Model A-705 flame ionization gas chromatograph. Peak areas were standardized with solutions of known molar amounts of the products. Relative reactivities were determined from the expression $k/k_0 = P/P_0$, where P is the moles of products from competing substituted styrene (**7b** and **7c**) and P_0 is the moles of products formed from styrene (**7a**).

C. Dimethylmethylidene (B) from 1-Bromo-2-methylpropene (5).—A mixture of 0.1 mol of substituted styrene, 0.1 mol of styrene, and 0.01 mol of *tert*-BuOK·*tert*-BuOH at −10° under nitrogen was treated dropwise with 0.01 mol of **5**[7] during 30 min. The mixture was stirred for an additional 1 hr at 0° and poured into water, and the organic products were extracted into ether. After drying, the ether was removed and the products were analyzed by vpc according to the method described in part B.

1-(2-Methylprop-1-enylidene)-2-phenylcyclopropane (3a) was obtained in 35% yield by treating styrene with 1-bromo-3-methylbuta-1,2-diene and *tert*-BuOK·*tert*-BuOH according to the procedure described by Landor and Whiter.[4]

1-(2-Methylprop-1-enylidene)-2-(4-chlorophenyl)cyclopropane (3c) was prepared in 30% yield by the above procedure[4] except that 4-chlorostyrene was used: bp 98–99° (0.5 mm); $n^{26}D$ 1.5681; ir (neat) 2020 cm^{-1} (allene); nmr (CCl_4) multiplets at τ 2.65 and 2.82 (4 H, aromatic peaks), 7.3 (1 H, four peaks, CH). 7.8–9.0 with a sharp peak at 8.20 (8 H, CH_2 and CH_3). *Anal.* Calcd for $C_{13}H_{13}Cl$: C, 76.1; H, 6.3; Cl, 17.6. Found: C, 76.3; H, 6.3; Cl, 17.3.

1-(2-Methylprop-1-enylidene)-2-(4-methylphenyl)cyclopropane (3b) was prepared as above in 49% yield except that 4-methylstyrene was used: bp 90–92° (0.4 mm); $n^{25}D$ 1.5509; ir (neat) 2020 cm^{-1} (allene); nmr (CCl_4) τ 3.05 (4 H, s, aromatic CH_3), 7.29 (1 H, four peaks, CH), 7.82 (3 H, s, CH_3) 8.0–9.0 with sharp singlet at 8.20 (8 H, CH_2 and CH_3). *Anal.* Calcd for $C_{14}H_{16}$: C, 91.8; H, 8.2. Found: C, 91.6; H, 8.1.

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[26] G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **4**, 41 (1967).

[27] F. Strauss, L. Kollek, and W. Heyn, *Ber.*, **63**, 1868 (1930).

[28] N. Nazarov and L. P. Bergelson, *Zh. Obshch. Khim.*, **27**, 1540 (1957); *Chem. Abstr.*, **52**, 3660 (1958).

[29] All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as an internal standard (τ 10). Ir spectra were recorded on a Perkin-Elmer Model 337 grating spectrometer. Spectra were calibrated with polystyrene film.

[30] A Varian M-66 mass spectrometer was used. We thank Dr. P. Gaspar, Chemistry Department, Washington University, St. Louis, Mo., for making arrangements for us to use the instrument.

Thermal Rearrangements of 1-(2-Methylprop-1-enylidene)-2-phenylcyclopropanes (3a–c). Method A.—A solution of 1.0 g of 1-(2-methylprop-1-enylidene)-2-arylcyclopropane and 10 ml of mesitylene was heated under reflux (163°) for 2 hr. The infrared spectrum showed complete absence of allene absorption at 2020 cm^{-1}. The product was isolated by short path distillation. Vpc analysis of the mesitylene solutions prior to distillation showed the presence of solvent, rearranged product, and less than 1% of unidentified materials which had long retention times. Isolated yields follow: **8a**, 89%; **8b**, 96%; **8c**, 91%.

Method B.—A 50-μl sample of **3a**, **b**, or **c** was injected onto a 5 ft × 0.25 in. column of 20% SE-30 on Chromosorb W (60/80) at 170°. The eluent was collected at −60°. In all cases, more than 45 μl (90%) of product was collected. Nmr and vpc analysis showed the material to be completely homogeneous.

The following physical and analytical properties were found. **8a:** bp 70–71° (0.25 mm); ir (neat) 1795 and 1740 cm^{-1};[31] nmr (CDCl$_3$) τ 2.84 (5 H, s, aromatic), 4.60 and 4.80 (1H each, rounded, vinyl), 7.00 (1 H, broad, benzylic), 7.97 and 8.12 (3 H each, broad singlets, CH$_3$). *Anal.* Calcd for $C_{13}H_{14}$: C, 91.7; H, 8.3. Found: C, 91.6; H, 8.3. **8b**: bp 98–99° (0.25 mm); ir (neat) 1800 and 1730 cm^{-1};[30] nmr (CDCl$_3$) τ 3.00 (4 H, aromatic), 4.46, 4.83 (1 H each, vinyl), 7.10 (1 H, broad, benzylic), 7.78 (3H, *p*-CH$_3$), 8.06, 8.17 (3 H each, allylic CH$_3$). *Anal.* Calcd for $C_{14}H_{16}$: C, 91.8; H, 8.2. Found: C, 92.0; H, 8.1. **8c:** bp 89–90° (0.25 mm); ir (neat) 1800 and 1740 cm^{-1};[31] nmr τ 2.5–3.0 (4 H, m, aromatic), 4.60, 4.75 (1 H each, vinyl), 7.10 (1 H, broad, benzylic), 7.95, 8.10 (3 H each, CH$_3$). *Anal.* Calcd for $C_{13}H_{13}Cl$: C, 76.1; H, 6.3; Cl, 17.6. Found: C, 76.0; H, 6.4; Cl, 17.7.

Rearrangement Rates for 3a–c.—The 2-phenylalkenylidenecyclopropanes were mixed with dry mesitylene to give solutions with allene absorbance in the infrared spectrum of about 0.5 using a 0.15-mm path length sodium chloride cell. Sealed steam-cleaned glass tubes containing the degassed solution were immersed in an oil bath maintained at 137 ± 1.5°. Samples were removed at various time intervals and the reaction was quenched at −60°. Absorbance values for the allene band at 2040 cm^{-1} were obtained in the 0.15 mm solution cell. An infinity reading was made about 24 hr after the initial reading. First-order rate plots were linear for the entire reaction. Rate constants were obtained from the expression $k = 0.693/t_{1/2}$, where $t_{1/2}$ is the half-life of the reaction in minutes. Rate constants obtained follow: **3c**, $1.9 \pm 0.1 \times 10^{-2}$ min^{-1}; **3b**, $1.7 \pm 0.1 \times 10^{-2}$ min^{-1}; **3a**, $1.5 \pm 0.1 \times 10^{-2}$ min^{-1}. Two runs were made on each reaction.

1-(Triethylsilyl)-3-methyl-1,2-butadiene (10) and 1-(Triethylsilyl)-3-methyl-1-butyne (11).—Potassium *tert*-butoxide–*tert*-BuOH (9.3 g, 0.05 mol) was added all at once to a stirred solution of **1** (7.3 g, 0.05 mol) and 20 ml of triethylsilane (Pierce Chemical Co.) in 50 ml of dry benzene. An exothermic reaction ensued. After 30 min the cooled reaction mixture was poured into cold water and extracted with ether. The organic solution was worked up in the usual manner and the ether was distilled. Short-path distillation of the remaining liquid yielded 7.9 g (68%) of **10**: bp 108–109° (20 mm); n^{19}D 1.4499; ir (neat) 1960 cm^{-1} (allene); nmr (CDCl$_3$) τ 7.3 (1 H, m, vinyl), 8.35 (6 H, d, allylic CH$_3$, $J \sim$ 4H), 8.8–9.8 (15 H, m, C$_2$H$_5$). *Anal.* Calcd for $C_{11}H_{22}Si$: C, 75.3; H, 12.1; Si, 12.6. Found: C, 75.1; H, 12.1; Si, 12.9.

A 0.5-ml sample of **10** was heated for 2 hr at 150–170° in a steam-cleaned, closed glass tube. Nmr analysis of the mixture showed the presence of a 2:1 mixture of **10** and 1-(triethylsilyl)-3-methyl-1-butyene (**11**). An analytical sample of **11** was obtained by preparative vpc: ir (neat) 2100 cm^{-1} (C≡C); nmr (CCl$_4$) τ 6.4 (1 H, m, CH), complex pattern at 8.6–9.8 (21 H) containing a doublet centered at 8.04 (CH$_3$, J = 6 Hz). *Anal.* Found: C, 75.2; H, 12.0.

Reaction of 1-Bromo-3-methyl-1,2-butadiene (1) with Methyllithium at −100°.—A solution of 7.4 g (0.05 mol) of **1** in 50 ml of dry tetrahydrofuran under a dry nitrogen atmosphere was cooled to −100° (liquid nitrogen–bromoethane). Ethereal methyllithium (1.0 *N*, 50 ml, 0.05 mol) was added dropwise over a period of 1 hr. A white solid appeared in the flask. After 0.5 hr, 50 ml of dry acetone was added rapidly. The mixture was allowed to warm to room temperature and was then extracted with ether. The ether extract was washed with potassium carbonate solution and saturated sodium chloride solution and then dried by filtration through magnesium sulfate. After removing the ether by distillation, the remaining liquid was distilled through a short-path apparatus, yielding 2-hydroxyl-2,5-dimethylhexa-3,4-diene (**15**, 6.5 g, 35%): bp 50–54° (20 mm); ir (neat) 3450 (broad OH), 1960 cm^{-1} (allene); nmr (CCl$_4$) τ 4.85 (1 H, m, vinyl), 8.17 (6 H, d, allylic CH$_3$, J = 2 Hz), 9.60 (6 H, s, CH$_3$). *Anal.* Calcd for $C_8H_{14}O$: C, 78.9; H, 9.9. Found: C, 78.7; H, 9.8.

1,1-Dibromo-3-methyl-1,2-butadiene (16) and 1,1-Dibromo-3-methyl-1,3-butadiene (17).—A mixture of 40.0 g (0.25 mol) of 1-bromo-3-methyl-1-butyn-3-ol (**15**), 200 ml of 48% hydrobromic acid, 32 g of cuprous bromide, 3.2 g of copper powder, and 32 g of sodium bromide was stirred at 27° for 1.5 hr. The mixture was filtered and the organic material was taken up in ether. After a usual work-up and removal of ether by distillation at atmospheric pressure, the remaining dark oil was subjected to short-path distillation. The first fraction obtained boiled at 72–78° (25 mm) and amounted to 11.5 g of approximately equal amounts of **16** and **17**. The presence of **16** in the mixture was determined by absorption bands in the nmr (sharp singlet at τ 8.0) and ir (1960 cm^{-1}) spectra. On standing at room temperature for several hours, **16** completely converted to **17**.

A second fraction boiling at 78–80° (25 mm) yielded 23.3 g of pure **17**. The total yield of **17** was 34.7 g (62%); n^{27}D 1.5601; ir (neat) 1601 cm^{-1} (C=C); nmr (CCl$_4$) τ 3.00 (1 H, broad singlet, vinyl), 4.84 (2 H, m, vinyl CH$_2$), and 7.96 (3 H, m, CH$_3$); mol wt 224 (mass spectrum).[32] *Anal.* Calcd for $C_5H_6Br_2$:[32] C, 26.5; H, 2.7; Br, 70.8. Found: C, 26.6; H, 2.5; Br, 70.9.

A mixture of *cis*- and *trans*-1,2-dibromo-3-methyl-1,3-butadiene (**19**) prepared by a described procedure[28] showed absorptions in its nmr spectrum (CCl$_4$) at τ 3.71 (vinyl CH), 4.75 (vinyl CH$_2$), and 8.00 (CH$_3$).

6,6-Dibromo-2-methylcyclohexene-*cis*-4,5-dicarboxylic Anhydride (18).—A mixture of 1,1-dibromo-3-methyl-1,3-butadiene (3.7 g, 16 mmol) and maleic anhydride (1.57 g, 16 mmol) in 20 ml of benzene was heated at reflux overnight. On cooling, 1.5 g (29%) of **18** crystallized, mp 264–265°. The nmr spectrum (acetone-d_6) showed peaks at τ 3.2 (1 H, vinyl), 6.0–6.6 (4 H, m, aliphatic), and 7.9 (3 H, m, CH$_3$). *Anal.* Calcd for $C_9H_8Br_2O_3$: C, 33.3; H, 2.5; Br, 49.4. Found: C, 33.0; H, 2.4; Br, 49.5.

Registry No.—A, 4209-13-6; B, 26265-75-8; **2a,** 100-42-5; **2b,** 622-97-9; **2c,** 1073-67-2; **3a,** 4544-23-4; **3b,** 32571-02-1; **3c,** 32571-01-0; **8a,** 30896-86-7; **8b,** 34220-33-2; **8c,** 34220-34-3; **10,** 34220-35-4; **11,** 34220-36-5; **14,** 2424-45-5; **17,** 34220-38-7; **18,** 34220-39-8.

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[31] R. F. Bleiholder and H. Shechter, *J. Amer. Chem. Soc.*, **86**, 5032 (1964), report 5.52 μ (1812 cm^{-1}) and 6.0 μ (1667 cm^{-1}) as characteristic absorptions for dimethylenecyclopropanes.

[32] The molecular weight and formula were determined by mass spectrometry at the Morgan–Schaffer Corp., Montreal, Canada.