# Insertion of Vinylidene Carbenes into Carbon–Hydrogen and Silicon–Hydrogen Bonds[1]

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Abstract: *n*-Alkyl vinylidene carbenes (or carbenoids) generated from 1-bromo-1,2-dienes and potassium *tert*-butoxide insert into the silicon–hydrogen bond of triethylsilane and into the carbon–hydrogen bond α to oxygen in 2,5-dimethyltetrahydrofuran and in primary alcohols (or alkoxides). In the last case mechanisms are suggested involving orientation of the vacant orbital of the carbene either by hydrogen bonding with the alcohol (Figure 1) or by complexation with the alkoxide (Figure 2) to account for the specificity and relatively high yield of the observed α insertion.

In the preceding paper,[2] evidence was presented suggesting that the reaction of 1-bromo-1-heptyne with sodium 2,2-dimethyl-1,3-dioxolane-4-methanolate proceeds, at least in part, through an intermediate zwitterion–carbene (1)[3a,b] giving four products, three of which (7, 8, and 9) are
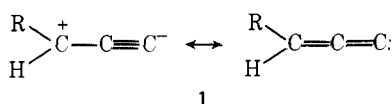
adequately explained in terms of the ambident electrophilic reactivity of **1** and a base-catalyzed prototropic rearrangement. The fourth and major product was the allenic alcohol **6**, which was tentatively assumed to be derived from insertion of the carbene into the carbon–hydrogen bond α to the oxygen of the alcohol or alkoxide.

While insertion of a variety of carbenes (or carbenoids) into carbon–hydrogen and silicon–hydrogen bonds is well established,[4a-c] to our knowledge, an unequivocal example of this phenomenon has not been reported for the resonance stabilized species **1**.[5] A concerted mechanism has been suggested as a possibility in the reaction of **1** with dimethyl malonate[6] or with 2-methyl-3-butyn-*N*-methyl carbamate;[7] however, in both cases electrophilic attack on the corresponding anion appears more likely.
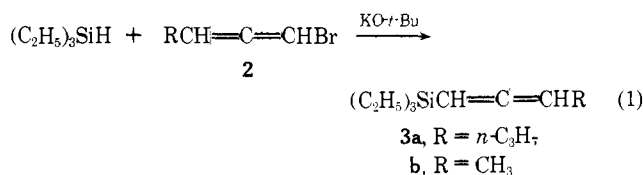
Very little precedent exists in carbene chemistry for the apparent specificity and high yield (relative to other presumably more favorable processes[3a]) observed herein for the C–H insertion α to the oxygen of alcohols or alkoxides. Although the mechanism of singlet carbene insertion is not at present unequivocal, C–H bonds at positions capable of stabilizing a partial positive charge in the transition state are especially reactive.[4a-c] Seyferth and coworkers[8-10] have extensively investigated the reaction of dichlorocarbene with a variety of hydrocarbons, ethers and silanes, finding 2,5-dimethyltetrahydrofuran and triethylsilane to be the most reactive of the compounds studied. Similarly, Newman and Beard[11] obtained high yields of vinyl silanes by reaction of alkylidene carbenes ($R_2C{=}C{:}$) with triethylsilane. In this case, insertion was faster than addition to cyclohexene. Accordingly, the present investigation was initiated to gain insight into single bond reactions of vinylidene carbenes and to further clarify the interaction of **1** with alcohols (or alkoxides).

Vinylidene carbenes have been generated fom 3-halo-1-alkynes,[12] 3-acetoxy-1-alkynes,[13] diazoallenes,[14] 1-halo-1,2-dienes,[15] and recently from 1-bromo-1-alkynes.[2] Preliminary studies established 1-bromo-1,2-dienes as the most convenient starting materials for monoalkylvinylidene carbenes. 2,5-Dimethyltetrahydrofuran (DMTHF) and trieth-
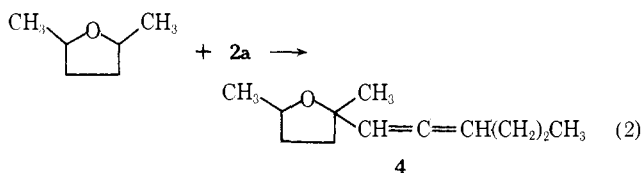
ylsilane (TES) were chosen to represent compounds possessing reactive C–H and Si–H bonds, respectively.

Results and Discussion

Reaction of equimolar quantities of 1-bromo-1,2-hexadiene (**2a**) and potassium *tert*-butoxide in the presence of a 10 *M* excess of triethylsilane in refluxing benzene solution gave a 33% yield of the allenyl silane **3a**. In a similar manner **3b** was prepared from 1-bromo-1,2-butadiene (**2b**) in 29% yield (eq 1). No spectral evidence was found for the presence of isomeric acetylenes.

$$(C_2H_5)_3SiH + RCH{=}C{=}CHBr \xrightarrow{KO\text{-}t\text{-}Bu}$$

$$\begin{array}{c} 2 \end{array}$$

$$(C_2H_5)_3SiCH{=}C{=}CHR \quad (1)$$

$$\textbf{3a}, R = n\text{-}C_3H_7$$
$$\textbf{b}, R = CH_3$$

Carbon–hydrogen insertion products were not observed with cumene, tetrahydrofuran, and 1,2-dimethoxyethane. Reaction of **2a** with potassium *tert*-butoxide and DMTHF in refluxing benzene solution (eq 2) gave a 3% yield of **4**;

$$\text{CH}_3\text{—O—CH}_3 + \textbf{2a} \longrightarrow$$

$$\text{CH}_3\text{—O—CH}_3, \text{CH}{=}C{=}CH(CH_2)_2CH_3 \quad (2)$$

$$\textbf{4}$$

the presence of only one hydrogen (nmr) in the ether region showed that attack occurred α to oxygen.[16]
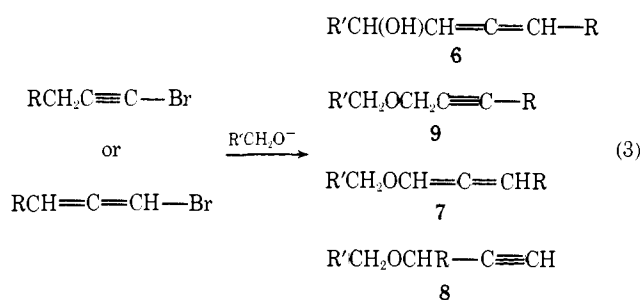
Evidence was presented in the preceding paper[2] that 1-bromo-1-alkynes are also precursors of **1**, perhaps by rearrangement to the isomeric 1-bromo-1,2-diene. A comparison of the reactions of 1-bromo-1-hexyne and 1-bromo-1,2-hexadiene (**2a**) with the sodium salts of 2-methoxyethanol, 3-methoxy-1-propanol, 1-butanol, and 2,2-dimethyl-1,3-dioxolane-4-methanol in refluxing benzene solution revealed essentially identical product ratios in each case as expected for a common intermediate (see Table I).[17] Yields were generally higher when using 1-bromo-1,2-dienes; this may be attributed to competing nucleophilic attack on bromine in the 1-bromo-1-alkynes.[2] Four products were obtained in each of these reactions (eq 3) with the allenic alcohol **6** being the major component (Table I). When the reaction was repeated in the presence of cyclohexene, the total yield of the products **6**, **7**, **8**, and **9** was greatly decreased while the relative ratios were unchanged suggesting that all were derived, directly or indirectly, from the carbene (the

Table I. Formation of Allenic Alcohols from 1-Bromo-1-alkynes and 1-Bromo-1,2-dienes
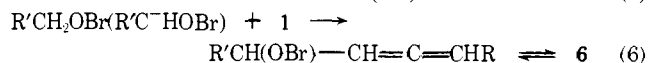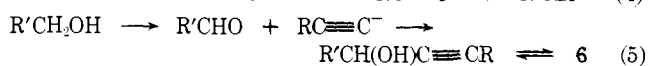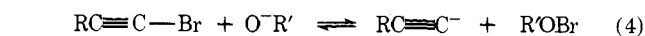
	R—CH(OH)—CH=C=CH—R¹ 6		% yield of 6 (Total yield of 6, 7, 8, 9)[a]	
			From R¹CH₂C≡CBr	From R¹CH=C=CHBr
	R	R¹		
(a)	$-CH_2OCH_3$	$-(CH_2)_2CH_3$	9 (15)	13 (26)
(b)	$-(CH_2)_2OCH_3$	$-(CH_2)_2CH_3$	4 (7)	5 (12)
(c)	$-(CH_2)_3CH_3$	$-(CH_2)_2CH_3$	4 (8)	6 (13)
(d)	$-CHO \quad CH_3$ $\times$ $CH_2-O \quad CH_3$	$-(CH_2)_2CH_3$	8 (14)	b

[a] The yields were determined by glpc using the internal standard technique. [b] The reaction with 1-bromo-1,2-heptadiene was not investigated.

major product was the allenic cyclopropane arising from trapping of **1** by cyclohexene[2]). Acetylation of the crude reaction mixture produced stable allenic acetates derived from **6** and did not affect the other products.

$$R'CH(OH)CH=C=CH—R$$
$$6$$

$$RCH_2C\equiv C—Br$$
$$or \qquad \xrightarrow{R'CH_2O^-} \qquad R'CH_2OCH_2C\equiv C—R$$
$$9 \qquad\qquad (3)$$
$$RCH=C=CH—Br \qquad\qquad R'CH_2OCH=C=CHR$$
$$7$$

$$R'CH_2OCHR—C\equiv CH$$
$$8$$

Although the proposed insertion reaction α to the oxygen of primary alcohols (alkoxides) appears feasible, alternative mechanisms leading to the same product **6** must be considered. One such mechanism involves the intermediate formation of aldehyde. As positive bromine in 1-bromo-1-alkynes is a potential oxidant, treatment with alkoxide may establish an equilibrium condition[3a] (eq 4) with the generation of

$$RC\equiv C—Br + O^-R' \rightleftharpoons RC\equiv C^- + R'OBr \qquad (4)$$
$$R'CH_2OH \longrightarrow R'CHO + RC\equiv C^- \longrightarrow$$
$$\qquad\qquad R'CH(OH)C\equiv CR \rightleftharpoons 6 \qquad (5)$$
$$R'CH_2OBr(R'C^-HOBr) + 1 \longrightarrow$$
$$\qquad R'CH(OBr)—CH=C=CHR \rightleftharpoons 6 \qquad (6)$$

a hypobromite. Oxidation of the original alcohol to aldehyde followed by reaction with **1** or acetylide ion (with subsequent rearrangement) is plausible (eq 5) as is attack by **1** at the α-methylene position of the postulated hypobromite (or its anion) (eq 6). Neither of these pathways to **6** should be favored when bromodienes are employed; in fact, (Table I), the ratio of products was unchanged while the yield doubled suggesting that hypobromites are not involved. Preliminary interconversion of bromodiene to bromoacetylene is unlikely as glpc showed the reaction with bromodiene to be complete within 5 min, whereas the bromoacetylene reaction was less than 1% complete in the same time. Adding n-butyraldehyde to several of the reaction mixtures produced no cross-over product and did not increase the yield of **6c** in the case of 1-butanol, offering further evidence against a free aldehyde intermediate.
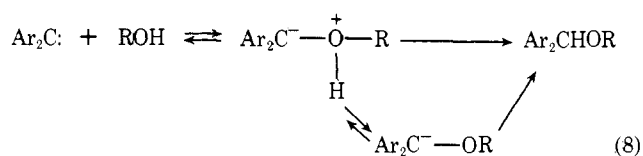
Another possible route to **6** is a Wittig rearrangement[18] of either **7** or (followed by propargylic rearrangement[19]) of **8** or **9** under the vigorous reaction conditions (eq 7). Treat-

$$RCH_2OR' \xrightarrow{base} RC^-HOR' \longrightarrow RCH(OH)R' \qquad (7)$$
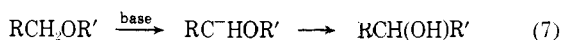
ment of each of the compounds **7, 8,** and **9** with a variety of bases using (a) the reaction conditions of eq 3, (b) potassium tert-butoxide in refluxing toluene, or (c) n-butyllithium in refluxing tetrahydrofuran, failed to effect a rearrangement suggesting that **6** is not derived from any of the other products by thermal or base-catalyzed processes under conditions favorable to the Wittig rearrangement.[18]

The mechanism of singlet carbene insertion[4a-c] involving a triangular transition state[20,21] has recently been supported by new experimental evidence[22] and the additional corollary suggested that attack occurs midway between and perpendicular to the C–H bond.[22] However, an alternative explanation[23] suggesting that the hydrogen atom is the focus of attack, rather than the electrons of the C–H bond, has been put forward based on extended Hückel calculations.[24]

A second mechanistic alternative for the formation of **6** could be an initial O–H insertion reaction[4c,25] to give an ylide intermediate[25,26] followed by a Wittig rearrangement. Bethell[25a] has recently proposed an ylide mechanism and an α-alkoxycarbanion for the reaction of diphenylcarbene with alcohol (eq 8) concluding that proton transfer between oxy-

$$Ar_2C: + ROH \rightleftharpoons Ar_2C^-—\overset{+}{O}—R \longrightarrow Ar_2CHOR$$
$$\qquad\qquad\qquad\qquad | \qquad\qquad\qquad \nearrow$$
$$\qquad\qquad\qquad\qquad H \qquad\qquad \nearrow$$
$$\qquad\qquad\qquad\qquad\searrow Ar_2C^-—OR \qquad (8)$$

gen atoms is more rapid than transfer from oxygen to carbon.[25b] However, an extension of this hypothesis to our results cannot explain the formation of the allenic alcohol (**6**), since an α-alkoxycarbanion [$RCH_2O—\bar{C}=C=C$] in this case would be expected to give the enolate of an α,β-unsaturated ketone [$\bar{O}—C(CH_2R)=C=C$] on Wittig rearrangement. In addition, treatment of the allenic ether with n-butyllithium, conditions which have been reported to readily yield the anion ($O—\bar{C}=C=C$) in other investigations,[28] did not effect a rearrangement. Similarly, direct formation of the anion by reaction of the carbene with alkoxide would not be expected to give the allenic alcohol.

A modification involving stepwise ylide formation, 1,3-proton shift, and subsequent Wittig rearrangement could, however, account for the formation of **6** (Scheme I). If this is the case there is no reason why ylide formation would not also facilitate an analogous reaction with the corresponding methyl ether; since no insertion α to the ether oxygen was in fact observed in 1,2-dimethoxyethane or 2-methoxyethanol we conclude that, although the ylide mechanism and rear-
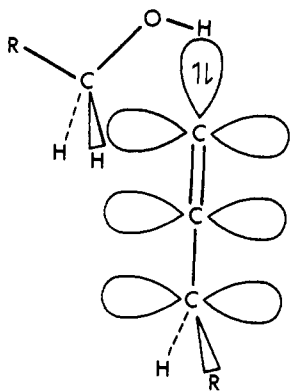
Scheme I
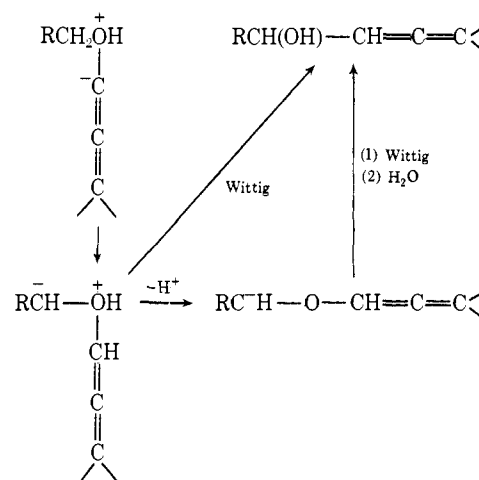
Figure 1. Hydrogen-bonded complex between zwitterion–carbene and alcohol.
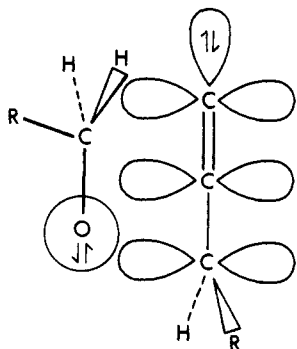

Figure 2. Anion–carbene pair from alkoxide ion and orbital at C-3.

rangement cannot be rigorously excluded, this mechanism is unlikely in the present investigation.

Vinylidene carbenes are unique in that the terminal or "carbene" carbon atom has considerable carbanionic character derivable from ionic contributions to the resonance hybrid. In the presence of alcohol, hydrogen bonding between the alcohol and the free electron pair would be expected and could orient the empty orbital at C-1[29] in close proximity to the C–H bond α to hydroxyl and thereby facilitate insertion (Figure 1). Inspection of models confirms the feasibility of such a process. The geometry of the postulated complex could accommodate an insertion reaction occurring either by attack on the electrons of the C–H bond or on the hydrogen atom. However, we prefer the former and a triangular transition state is depicted in Figures 1 and 2. The geometry of such a complex could increase the rate of α C–H insertion or alternatively perturb (presumably decrease) the relative rates of competing allenic and propargylic ether formation in benzene containing small quantities of alcohol.[8,30,31]

Vinylidene carbenes also have carbonium ion character and may complex with an alkoxide ion through the vacant orbital at C-3. This type of anion–carbene pair directs the empty orbital at C-1 into close proximity to the C–H bond α to oxygen of the alkoxide ion and thus may facilitate insertion (Figure 2). In this connection, the question of whether vinylidene carbenes are free carbenes or carbenoids[32] is of obvious interest. Noble, et al.,[33] have presented evidence that the reactive species in the solvolysis of 1-chloro-3-methyl-1,2-butadiene is an anion–carbene pair in which the chloride ion is complexed with the empty orbital at C-3, which is essentially equivalent to the alkoxide–carbene pair represented in Figure 2. In contrast, Jones[14] and Hartzler[34] have independently offered evidence that vinylidene carbenes are not complexed in alkene addition. The available data do not permit clear distinction between these

possibilities although we prefer the alcohol–carbene complex (Figure 1).[35]

A few carbene insertions α to alcohols have been reported.[36] Photolysis of diazomethane[37] or ethyl diazoacetate[38] in methanol gave a small yield of C–H insertion product. Similarly, Gunning and coworkers[39] reported the insertion of carbomethoxymethylene into the tertiary C–H bond of 2-propanol in 9% yield. It is tempting to suggest a similar hydrogen-bonded complex in the case of carbomethoxymethylene; and indeed inspection of models suggests that hydrogen bonding between the alcohol and the carbonyl oxygen directs the empty orbital so as to favor α C–H insertion.

Experimental Section[40]

General. Triethylsilane (PCR Inc.) and 2,5-dimethyltetrahydrofuran (DMTHF) (Aldrich Chemical Co.) were distilled from calcium hydride and stored over molecular sieves. Nmr and glpc indicated that DMTHF was a mixture of cis and trans isomers. Potassium tert-butoxide was purchased from Matheson Coleman and Bell and used without purification. All reactions were carried out in an atmosphere of prepurified nitrogen. Glpc yield determinations were made using the internal standardization technique. The instruments and general conditions have been described.[2] Analytical glpc determinations were made on a 6 ft × ⅛ in. glass column packed with 3% carbowax 20M on 100–120 mesh Chromosorb W. All preparative glpc separations were made on a 10 ft × ⅜ in. aluminum column packed with 10% QF-1 on 40–60 mesh Chromosorb W using helium flow rates of 120–140 ml/min (column A).

1-Bromo-1,2-butadiene (**2b**) and 1-bromo-1,2-hexadiene (**2a**) were prepared by the procedure of Landor.[41] Nmr and glpc analysis of **2a** and **2b** showed the presence of 5–7% of the isomeric 3-bromo-1-acetylene as reported.[41] This material was used without further purification and no correction in yield was made for the impurity, as the behavior of secondary 3-bromoacetylenes under these conditions has not been established.

Reaction of 1-Bromo-1,2-hexadiene (2a) with Potassium tert-Butoxide and DMTHF. **2a** (4.0 g, 0.0248 mol) was added dropwise (5 min) to 2.76 g (0.025 mol) of potassium tert-butoxide dissolved in a mixture of 75 ml of benzene and 35 g of DMTHF maintained at 80° in an oil bath. After completion of addition the reaction mixture was heated for 10 min, cooled, filtered, and worked up as usual. After removing the solvents through a short column (150 mm), distillation afforded 0.150 g (3%) of crude 2,5-dimethyl-2-(1′,2′-hexadienyl)tetrahydrofuran (**4**), bp 45–53° (4 mm). Glpc indicated a mixture of isomers as expected which were collected together to give the analytical sample (column A, 120°): ir (neat) 1955, 1105, and 870 cm⁻¹; nmr (CDCl₃) δ 5.18 (m, 2 H, CH=C=CH), 4.07 (m, 1 H, OCH), and 2.4–0.8 ppm (broad m, 17 H, CH). A tarry residue remained in the flask after distillation which gave no identifiable product.

Anal. Calcd for C₁₂H₂₀O (180.3): C, 79.94; H, 11.18; mol wt, 180. Found: C, 79.76; H, 11.13; mol wt (mass spectrum), 180.

Reaction of 1-Bromo-1,2-dienes with Potassium tert-Butoxide and Triethylsilane. General Procedure. A 10 M excess of triethylsilane and benzene (two volume ratio) were placed in a three-necked flask of appropriate size, equipped with reflux condenser, dropping funnel, nitrogen inlet, and magnetic stirring. Potassium tert-butoxide (0.05 mol) was added and the solution was heated to a gentle reflux. The bromodiene (0.05 mol) in 10 ml of benzene was added rapidly so as to maintain reflux (usually required 5–10 min). After completion of addition, heating was continued for 15 min and then the reaction mixture was cooled in an ice bath. After the usual work-up, the solvents were removed through a short column at 150 mm. Distillation of the residual oil afforded the crude allenyl silane which was then obtained in analytical purity by glpc. Small quantities of nonvolatile residue remained after distillation. The allenyl silanes obtained in this manner were of ca. 90% purity and contained two unidentified components of longer retention time on a carbowax column. The absolute yield of these impurities was approximately 1–2% each. Ir analysis of these impurities showed no allene or acetylene band. One of these compounds had a glpc retention time identical with a small impurity originally pres-

ent in the commercial triethylsilane.

1-Triethylsilyl-1,2-hexadiene (3a). 3a was prepared by the general procedure from 8.05 g of **2a**, 5.60 g of potassium *tert*-butoxide, and 54 g of triethylsilane in 33% yield, bp 77–80° (2 mm). The analytical sample was obtained by glpc (column A, 105°): ir (neat) 1950, 1918, 855, and 725 cm⁻¹; nmr (CDCl₃) δ 4.72 (m, 2 H, CH=C=CH), 1.95 (m, 2 H, C=C=CCH₂), and 1.65–0.3 ppm (broad m, 2 H, CH).

Anal. Calcd for C₁₂H₂₄Si (196.4): C, 73.38; H, 12.32; mol wt, 196. Found: C, 73.14; H, 12.17; mol wt (mass spectrum), 196.

1-Triethylsilyl-1,2-butadiene (3b). 3b was prepared from 6.65 g of **2b**, 5.60 g of potassium *tert*-butoxide, and 54 g of triethylsilane in 29% yield, bp 55–60° (19 mm). The analytical sample was obtained on column A, 80°: ir (neat) 1950, 1020, 860, and 725 cm⁻¹; nmr (CDCl₃) δ 4.90–4.50 (m, 2 H, CH=C=CHSi), 1.60 (q, 3 H, C=C=CCH₃), and 1.4–0.4 ppm (m, 15 H, CH).

Anal. Calcd for C₁₀H₂₀Si (168.4): C, 71.93; H, 11.98; mol wt, 168. Found: C, 71.86; H, 11.86; mol wt (mass spectrum) 168.

Reaction of 1-Bromo-3-methyl-1,2-butadiene with Potassium *tert*-Butoxide and Triethylsilane. As in the general procedure, 7.35 g (0.05 mol) of 1-bromo-3-methyl-1,2-butadiene⁴ⁱ was added to 5.60 g of potassium *tert*-butoxide and 54 g of triethylsilane. After work-up, distillation gave a major product, bp 71–80° (9 mm), which appeared to be largely the expected allenyl silane (~15% yield), but was, however, contaminated with an unknown impurity from which it could not be resolved on any of our glpc columns. A strong ir band at 1952 cm⁻¹ suggested the allene structure. Weak variable absorptions at 3425 and 2160 cm⁻¹ were noted for the impurity: nmr (CDCl₃) δ 4.65 (m, 2 H, C=C=CHSi), 1.62 (d, 6 H, J = 4 Hz (CH₃)₂C=C=C), and 1.35–0.4 ppm (m, CH). A singlet at 1.48 ppm of variable intensity was attributed to the impurity. Further attempts at purification were not made as a systematic investigation of dimethylvinylidene carbenes was not planned.

Reaction of 2b with Sodium 2-Methoxyethanolate. 2b (9.0 g, 0.0677 mol) was added dropwise (10 min) to a solution of 0.0677 mol of sodium 2-methoxyethanolate (prepared from 1.56 g of sodium and 5.15 g of 2-methoxyethanol) in 75 ml of benzene at 80°. The mixture was heated for 30 min, cooled, and worked up as usual. Glpc indicated the presence of three components⁴² with shorter retention times (not characterized) and a pair of partially resolved peaks attributed to the diastereoisomeric allenic alcohols. The solution was concentrated by distillation of solvent through a short column and treated with an excess of acetic anhydride and pyridine at room temperature for 48 hr. After hydrolysis and work-up, glpc confirmed the disappearance of the alcohol peaks and appearance of two partially resolved allenic acetate peaks of longer retention times. This material was isolated by glpc to give 1-methoxy-3,4-hexadien-2-yl acetate (column A, 135°): ir (neat) 1985 (C=C=C) and 1755 cm⁻¹ (COOR); nmr (CDCl₃) δ 5.50–4.90 (m, 3 H, CHOAc, CH=C=CH), 3.48 (d, 2 H, J = 5 Hz, CH₂O), 3.33 (s, 3 H, OCH₃), 2.05 (s, 3 H, CH₃COOR), and 1.65 ppm (m, 3 H, C=C=CCH₃).

Anal. Calcd for C₉H₁₄O₃: C, 63.51; H, 8.29. Found: C, 63.28; H, 8.46.

Reaction of 2b and Sodium 3-Methoxy-1-propanolate. As in the preceding section, 1-methoxy-4,5-octadien-3-yl acetate was obtained from 20 g (0.124 mol) of **2b** and 0.124 mol of sodium 3-methoxy-1-propanolate in refluxing benzene solution and subsequent acetylation with acetic anhydride in pyridine. After removal of solvents the product³³ was obtained by glpc (column A, 135°): ir (neat) 1980 (C=C=C), 1755 (COOR), 1240, and 1122 cm⁻¹; nmr (CDCl₃) δ 5.25 (m, 3 H, CHOAc, CH=C=CH), 3.40 (t, 2 H, J = 6 Hz, CH₂O), 3.28 (s, 3 H, OCH₃), 2.00 (s, 3 H, CH₃COO), and 1.98–0.75 ppm (broad m, 9 H, CH).

Anal. Calcd for C₁₂H₂₀O₃ (212.3): C, 67.89; H, 9.50. Found: C, 67.67; H, 9.39.

Reaction of 2b and Sodium *n*-Butoxide. 4,5-Decadien-7-yl acetate was prepared from 20 g of **2b** and 11.96 g of sodium *n*-butoxide as outlined above and isolated by glpc (column A, 145°): ir (neat) 1975 (C=C=C), 1750 (COOR), 1232, and 1018 cm⁻¹; nmr (CDCl₃) δ 5.25 (m, 3 H, CHOAc, CH=C=CH), 2.00 (s, 3 H, CH₃COOR), 2.11 (m, 2 H, C=C=CCH₂), and 1.75–0.79 ppm (broad m, 12 H, CH).

Anal. Calcd for C₁₂H₂₀O₂ (196.3): C, 73.43; H, 10.27. Found: C, 73.66; H, 10.36.

References and Notes

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(5) (a) After this work was completed, the reaction of dimethylvinylidene with triethylsilane was reported to give insertion into the Si–H bond: T. B. Patrick, E. C. Haynie, and W. J. Probst, *J. Org. Chem.*, **37**, 1553 (1972).
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Laboratory, University of California, Berkeley, Calif., or Alfred Bernhardt, Mülheim (Ruhr), West Germany. The phrase "worked up as usual" means that an ether–benzene solution of the products was washed with dilute alkali and/or acid, with water, and with saturated sodium chloride solution and dried over anhydrous sodium sulfate. After filtration the solvents were removed in vacuo.

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Rearrangement Reactions of 9-Arylbicyclo[4.2.1]nona-2,4,7-trien-9-yl Cations[1,2]

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Abstract: The preparations of the *syn*-9-phenyl- and 9-*p*-anisylbicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-nitrobenzoate esters are reported. Rate comparisons of these compounds with their fully saturated analogs reveal a decrease in the amount of π participation accompanying the reaction as the positive charge at the 9-carbon is increasingly stabilized by the nature of the aryl group. The products are completely rearranged and consist of 78% *exo*- and 12% *endo,cis*-2-dihydroindenyl alcohol plus *ca*. 10% indene with the aryl group always on the 2-carbon of the indenyl system.

The ionization reactions of *syn*-bicyclo[4.2.1]nona-2,4,7-trienyl *p*-toluenesulfonate derivatives (I-OTs) have been reported to yield only rearranged products.[3,4] A quantitative study of the acetolysis of I-OTs (Z = H) revealed the highly specific nature of the reaction. Thus, *cis,exo*-dihydroindenyl acetate (II-OAc) is effectively the only product formed (99%), and in the deuterated analog (Z = D) the deuterium label is found exclusively at C-2 of II-OAc.[4] This same pathway is operative under nonsolvolytic conditions. The decomposition of 9-deuterio-I-OTs in DMSO yields 2-deuterioindene in 74% yield.[3a] Earlier reports on the reactions with the 9-phenyl derivatives of I in aprotic solvents also indicate the production of rearranged products only. However, in these cases not only is the 2-phenylindene formed but also 8-phenylindenyl derivatives which are generated by a rearrangement involving a simple 1,2 shift.[5] Presumably, this pathway becomes accessible when the incipient positive charge at C-9 of I becomes stabilized by the presence of the phenyl substituent. On the other hand, it is not clear as to what extent the variation in the rearranged products is due to the difference in the reaction conditions. In order to resolve this situation and further develop our understanding of these rearrangement reactions it seemed important to study quantitatively the reactions of 9-aryl derivatives of I in conditions which permit direct comparison of the results with those from the unsubstituted compounds.

Results

Synthesis. The bicyclo[4.2.1]nona-2,4,7-trienone was prepared in the reaction between cyclooctatetraene dianion and dimethylcarbamyl chloride as previously described.[3,4] Treatment of the ketone with NaBH₄ produced the endo-carbinol I-OH (Z = H). The endo-carbinol III-OH was produced in the reaction with LiAlH₄ as previously described.[4,6] Hydrogenation of I-OH on Pt produced (endo) IV-OH in high yields. Treatment of the ketone with NaBD₄ (99% D) produced I-OH (Z = D) in 77% yield. The corresponding alkyl toluenesulfonate esters were prepared with *p*-toluenesulfonyl chloride in pyridine in the usual way.

syn-9-Hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (I-OH, Z = Ph) was similarly prepared in the reaction between cyclooctatetraene dianion and methyl benzoate. The

purified carbinol was obtained in 46% yield, mp 104.8–105.2 (lit.[3b] 105–107°). Hydrogenation of the carbinol with Pd produced the fully reduced endo analog, IV-OH (Z = Ph), in 97% yield, mp 59.0–59.5° (lit.[3a] 59°). The *p*-anisyl substituted analog I-OH (Z = *p*-An) was prepared in a similar way starting with *p*-methoxybenzoic acid methyl ester. The endo-trienyl carbinol, mp 129.0–129.5°, was obtained in 48% yield. Hydrogenation of the trienyl carbinol with Pt produced the saturated endo carbinol IV-OH (Z = *p*-An) in 96% yield, mp 92.0–93.0°. The corresponding *p*-nitrobenzoate esters (ROPNB) were prepared in the usual manner. Structure proofs are based on nmr and glc analysis primarily.

I-OH
Z = H, Ph, *p*-An

exo-II-OH
Z = H, Ph, *p*-An

III-OH

IV-OH
Z = H, Ph, *p*-An
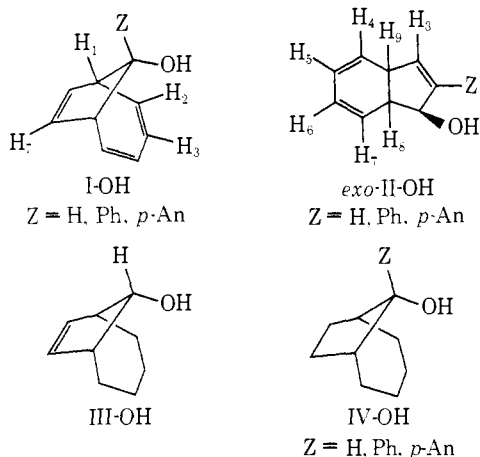
Rates. The rates of solvolysis of the various alkyl esters were followed by titration of the produced acid. Good first-order kinetics were observed in most cases, with the infinity titers being 99.5%. In the case of IV-OPNB (Z = Ph) the reaction is too slow to be practical, therefore the *k* value listed in Table I was estimated at 5% reaction and most likely reflects the acyl-oxygen cleavage reaction. At longer reaction times the *k* values increase rapidly, probably due to the H⁺-promoted reaction.

As previously discussed for the unsubstituted series, I-OTs is considerably more reactive than the more saturated analogs. On the other hand the presence of the anti double